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Methods for Chemical Analysis of Water and Wastes

(U.S.) Environmental Monitoring and Support
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Methods for Chemical Analysis of Water and Wastes

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METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES

March 1983

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OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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This third edition of "Methods for Chemical Analysis of Water and Wastes" contains the chemical analytical procedures used in U.S. Environmental Protection Agency (EPA) laboratories for the examination of ground and surface waters, domestic and industrial waste effluents, and treatment process samples. Except where noted under "Scope and Application," the methods are applicable to both water and wastewaters, and both fresh and saline water samples. The manual provides test procedures for the measurement of physical, inorganic, and selected organic constituents and parameters.

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FOREWORD

The accomplishment of our objective in protecting the environment requires a reliable assessment of the present condition and a determination of the effectiveness of corrective measures. Decisions which must be made on the need for pollution abatement and the most efficient means of achieving environmental quality depend upon the availability of sound data. Test procedures for measurement of the presence and concentration of substances hazardous to human health as well as an evaluation of the quality of the environment are essential to satisfactory decision-making.

This manual of chemical methods was prepared by the staff of the Environmental Monitoring and Support Laboratory of the Environmental Research Laboratory, Cincinnati to provide procedures for monitoring water supplies, waste discharges, and the quality of ambient waters. These test methods have been carefully selected to meet the needs of Federal Legislation and to provide guidance to laboratories engaged in protecting human health and the aquatic environment. The contributions and counsel of scientists in other EPA laboratories are gratefully acknowledged.

Test procedures contained herein, that are approved for water and waste monitoring under the Safe Drinking Water Act (SDWA) and the National Pollutant Discharge Elimination System (NPDES), of PL 92-500 are so indicated at the bottom of each title page. These approved methods are also recommended for ambient monitoring needs of Section 106 and 208 of PL 92-500. Methods without this stated approval are presented for information only. Correspondence on these methods is invited.

Robert L. Booth

Robert L. Booth
Acting Director, Environmental Monitoring and
Support Laboratory, Cincinnati, Ohio 45268

ABSTRACT

This manual provides test procedures approved for the monitoring of water supplies, waste discharges, and ambient waters, under the Safe Drinking Water Act, the National Pollutant Discharge Elimination System, and Ambient Monitoring Requirements of Section 106 and 208 of Public Law 92-500. The test methods have been selected to meet the needs of federal legislation and to provide guidance to laboratories engaged in the protection of human health and the aquatic environment.

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INTRODUCTION

NOTE: *Since the first printing of this edition in March 1979, various editorial errors have been brought to our attention which have been corrected in this second printing. In addition, it has been found necessary to add to this printing an updated preservation and holding times table (Table 1), as well as six new methods. They are: under pH, Electrometrics (continuous monitoring), Method 150.2; under Metals, Inductively Coupled Plasma, 200.7; under Metals/Chromium: Hexavalent, Dissolved, Method 218.5; under Metals/Sodium: AA, Furnace, Method 273.2; under Inorganic, non-metallics/Acidity: Titrimetric (acid rain), Method 305.1; and under Organics, Organic Carbon, Total: UV Promoted, Persulfate, Oxidation, Method 415.2.*

These additions have been made so as to keep users of the manual current with the procedures the Agency uses in determining compliance with applicable water and effluent standards it has established.

Persons who already possess a copy of the 1979 edition of the manual and who wish to update it by including the cited additions need not request another copy. The new material is available as a separate volume, entitled, "Technical Additions to Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020," EPA-600/4-82-055, from ORD Publications, CERI, U.S. Environmental Protection Agency, Cincinnati, OH 45268.

This third edition of "Methods for Chemical Analysis of Water and Wastes" contains the chemical analytical procedures used in U.S. Environmental Protection Agency (EPA) laboratories for the examination of ground and surface waters, domestic and industrial waste effluents, and treatment process samples. Except where noted under "Scope and Application", the methods are applicable to both water and wastewaters, and both fresh and saline water samples. The manual provides test procedures for the measurement of physical, inorganic, and selected organic constituents and parameters. Methods for pesticides, industrial organic waste materials, and sludges are given in other publications of the Agency. The methods were chosen through the combined efforts of the EPA Regional Quality Assurance Coordinators, the staff of the Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, and other senior chemists in both federal and state laboratories. Method selection was based on the following criteria:

(1) The method should measure the desired property or constituent with precision, accuracy, and specificity sufficient to meet the data needs of EPA, in the presence of the interfering materials encountered in water and waste samples.

(2) The procedure should utilize the equipment and skills available in modern water pollution control laboratories.

(3) The selected method is in use in many laboratories or has been sufficiently tested to establish its validity.

(4) The method should be rapid enough to permit routine use for the examination of a large number of samples.

Instrumental methods have been selected in preference to manual procedures because of the improved speed, accuracy, and precision. In keeping with this policy, procedures for the Technicon AutoAnalyzer have been included for laboratories having this equipment available. Other continuous flow automated systems using these identical procedures are acceptable.

Intralaboratory and interlaboratory precision and accuracy statements are provided where such data are available. These interlaboratory statements are derived from interlaboratory studies conducted by the Quality Assurance Branch, Environmental Monitoring and Support Laboratory; the American Society for Testing Materials; or the Analytical Reference Service of the US Public Health Service, DHEW. These methods may be used for measuring both total and dissolved constituents of the sample. When the dissolved concentration is to be determined, the sample is filtered through a 0.45-micron membrane filter and the filtrate analyzed by the procedure specified. The sample should be filtered as soon as possible after it is collected, preferably in the field. Where field filtration is not practical, the sample should be filtered as soon as it is received in the laboratory.

Many water and waste samples are unstable. In situations where the interval between sample collection and analysis is long enough to produce changes in either the concentration or the physical state of the constituent to be measured, the preservation practices in Table I are recommended.

This manual is a basic reference for monitoring water and wastes in compliance with the requirements of the Federal Water Pollution Control Act Amendments of 1972. Although other test procedures may be used, as provided in the Federal Register issue of October 16, 1973 (38FR 28758) and in subsequent amendments, the methods described in this manual will be used by the Environmental Protection Agency in determining compliance with applicable water and effluent standards established by the Agency.

Although a sincere effort has been made to select methods that are applicable to the widest range of sample types, significant interferences may be encountered in certain isolated samples. In these situations, the analyst will be providing a valuable service to EPA by defining the nature of the interference with the method and bringing this information to the attention of the Director, Environmental Monitoring and Support Laboratory, through the appropriate Quality Assurance Coordinator.

SAMPLE PRESERVATION

Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes, or natural waters, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations may also adsorb onto surfaces (glass, plastic, quartz, etc.), such as, iron and lead. Biological changes taking place in a sample may change the valence of an element or a radical to a different valence. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition. Therefore, as a general rule, it is best to analyze the samples as soon as possible after collection. This is especially true when the analyte concentration is expected to be in the low *u*g/1 range.

Methods of preservation are relatively limited and are intended generally to (1) retard biological action, (2) retard hydrolysis of chemical compounds and complexes, (3) reduce volatility of constituents, and (4) reduce absorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration, and freezing.

The recommended preservative for various constituents is given in Table 1. These choices are based on the accompanying references and on information supplied by various Quality Assurance Coordinators. As more data become available, these recommended holding times will be adjusted to reflect new information. Other information provided in the table is an estimation of the volume of sample required for the analysis, the suggested type of container, and the maximum recommended holding times for samples properly preserved.

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TABLE 1

RECOMMENDATION FOR SAMPLING AND PRESERVATION OF SAMPLES ACCORDING TO MEASUREMENT(1)

Measurement	Vol. Req. (ml)	Container[2]	Preservative[3,4]	Holding Time[5]
100 Physical Properties				
Color	50	P,G	Cool, 4°C	48 Hrs.
Conductance	100	P,G	Cool, 4°C	28 Days
Hardness	100	P,G	HNO_3 to $pH<2$	6 Mos.
Odor	200	G only	Cool, 4°C	24 Hrs.
pH	25	P,G	None Req.	Analyze Immediately
Residue				
Filterable	100	P,G	Cool, 4°C	7 Days
Non-Filterable	100	P,G	Cool, 4°C	7 Days
Total	100	P,G	Cool, 4°C	7 Days
Volatile	100	P,G	Cool, 4°C	7 Days
Settleable Matter	1000	P,G	Cool, 4°C	48 Hrs.
Temperature	1000	P,G	None Req.	Analyze Immediately
Turbidity	100	P,G	Cool, 4°C	48 Hrs.
200 Metals				
Dissolved	200	P,G	Filter on site HNO_3 to $pH<2$	6 Mos.
Suspended	200		Filter on site	6 Mos.(6)
Total	100	P,G	HNO_3 to $pH<2$	6 Mos.

TABLE 1 (CONT)

Measurement	Vol. Req. (ml)	Container[2]	Preservative[3,4]	Holding Time[5]
Chromium^{+6}	200	P,G	Cool, 4°C	24 Hrs.
Mercury				
Dissolved	100	P,G	Filter HNO_3 to $pH < 2$	28 Days
Total	100	P,G	HNO_3 to $pH < 2$	28 Days
300 Inorganics, Non-Metallics				
Acidity	100	P,G	Cool, 4°C	14 Days
Alkalinity	100	P,G	Cool, 4°C	14 Days
Bromide	100	P,G	None Req.	28 Days
Chloride	50	P,G	None Req.	28 Days
Chlorine	200	P,G	None Req.	Analyze Immediately
Cyanides	500	P,G	Cool, 4°C NaOH to $pH > 12$ 0.6g ascorbic acid[6]	14 Days[7]
Fluoride	300	P,G	None Req.	28 Days
Iodide	100	P,G	Cool, 4°C	24 Hrs.
Nitrogen				
Ammonia	400	P,G	Cool,4°C H_2SO_4 to $pH < 2$	28 Days
Kjeldahl, Total	500	P,G	Cool, 4°C H_2SO_4 to $pH < 2$	28 Days
Nitrate plus Nitrite	100	P,G	Cool, 4°C H_2SO_4 to $pH < 2$	28 Days
Nitrate[9]	100	P,G	Cool, 4°C	48 Hrs.
Nitrite	50	P,G	Cool, 4°C	48 Hrs.

TABLE 1 (CONT)

Measurement	Vol. Req. (ml)	Container[2]	Preservative[3,4]	Holding Time[5]
Dissolved Oxygen				
Probe	300	G bottle and top	None Req.	Analyze Immediately
Winkler	300	G bottle and top	Fix on site and store in dark	8 Hours
Phosphorus				
Ortho-phosphate, Dissolved	50	P,G	Filter on site Cool, 4°C	48 Hrs.
Hydrolyzable	50	P,G	Cool, 4°C H_2SO_4 to $pH<2$	28 Days
Total	50	P,G	Cool, 4°C H_2SO_4 to $pH<2$	28 Days
Total, Dissolved	50	P,G	Filter on site Cool, 4°C H_2SO_4 to $pH<2$	24 Hrs.
Silica	50	P only	Cool, 4°C	28 Days
Sulfate	50	P,G	Cool, 4°C	28 Days
Sulfide	500	~~P~~,G	Cool, 4°C add 2 ml zinc acetate plus NaOH to $pH>9$	7 Days
Sulfite	50	P,G	None Req.	Analyze Immediately
400 Organics				
BOD	1000	P,G	Cool, 4°C	48 Hrs.
COD	50	P,G	Cool, 4°C H_2SO_4 to $pH<2$	28 Days
Oil & Grease	1000	G only	Cool, 4°C H_2SO_4 to $pH<2$	28 Days
Organic carbon	25	P,G	Cool, 4°C H_2SO_4 or HCl to $pH<2$	28 Days
Phenolics	500	G only	Cool, 4°C H_2SO_4 to $pH<2$	28 Days

TABLE 1 (CONT)

Measurement	Vol. Req. (ml)	Container[2]	Preservative[3,4]	Holding Time[5]
MBAS	250	P,G	Cool, 4°C	48 Hrs.
NTA	50	P,G	Cool, 4°C	24 Hrs.

1. More specific instructions for preservation and sampling are found with each procedure as detailed in this manual. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 31, p. 72–82 (1976) Method D-3370.

2. Plastic (P) or Glass (G). For metals, polyethylene with a polypropylene cap (no liner) is preferred.

3. Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

4. When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table 1, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

5. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of sample under study are stable for the longer time, and has received a variance from the Regional Administrator. Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample stability.

6. Should only be used in the presence of residual chlorine.

7. Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper before the pH adjustment in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

8. Samples should be filtered immediately on-site before adding preservative for dissolved metals.

9. For samples from non-chlorinated drinking water supplies conc. H_2SO_4 should be added to lower sample pH to less than 2. The sample should be analyzed before 14 days.

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COLOR

Method 110.1 (Colorimetric, ADMI)

STORET NOS.
00082 at pH 7.6
00083 at ORIGINAL SAMPLE pH

1. Scope and Application
   - 1.1 This method is applicable to colored waters and waste that have color characteristics significantly different from the yellow platinum-cobalt standard.
   - 1.2 A working range of 25 to 250 color units is recommended. Sample values above 250 units may be determined by quantitative dilution.
2. Summary of Method
   - 2.1 This method is an extension of the Tristimulus Filter Method[1]. Tristimulus values are converted to an ADMI single number color difference, of the same magnitude assigned to platinum-cobalt standards, using the Adams Nickerson Color Difference (DE).
   - 2.2 Tristimulus values obtained by Spectrophotometric Method 204B[1] may be used to calculate ADMI values as outlined in this procedure under Calculation 9.2.
3. Interferences
   - 3.1 Since very slight amounts of turbidity interfere with the determination, turbid samples must be filtered prior to analysis. The optimum filter media to remove turbidity without removing color has not been found. Membrane and glass fiber filters with functional pore sizes of approximately 0.45 *u* are convenient to use. Other techniques such as centrifuging and/or filter aids may be used.
4. Sample Handling and Preservation
   - 4.1 Since biological activity may change the color characteristics of a sample, the determination should be made as soon as possible. Refrigeration at 4°C is recommended.
5. Calibration
   - 5.1 Standard curves must be established (as outlined in Procedure 8.3) for each photometer used, and are not interchangeable. For color values less than 250, a 5 cm cell path is recommended. Less than 5 cm cell paths may be used if calibration is performed with the shorter cell.
6. Apparatus
   - 6.1 Spectrophotometer or filter photometer capable of transmission measurements using tristimulus filters listed below:

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Filter number	Wavelength of maximum transmittance in nm	Corning designation*
1	590	CS 3–107
2	540	CS 4–98
3	438	CS 5–70

*Available from Corning Glass Works, Optical Products Department, Corning, NY 14830.

7. Reagents

7.1 Standard chloroplatinate solution: Dissolve 1.246 g potassium chloroplatinate, K_2PtCl_6, (equivalent to 0.500 g metallic Pt) and 1 g crystalline cobaltous chloride, $CoCl_2 \cdot 6H_2O$, in distilled water containing 100 ml of conc. HCl. Dilute to 1000 ml with distilled water. This standard solution is defined as 500 ADMI color units.

7.2 Sulfuric acid, concentrated.

7.3 Sodium hydroxide, 10 N: Dissolve 40 g of sodium hydroxide in 80 ml of distilled water. Cool to room temperature and dilute to 100 ml with distilled water.

8. Procedure

8.1 Prepare two 100 ml volumes of sample by maintaining the original pH of one aliquot and adjusting the second aliquot as necessary to pH 7.6 with sulfuric acid (7.2) or sodium hydroxide (7.3).

8.2 Filter samples to remove turbidity through a 0.45 *u* membrane filter, glass fiber filter or other suitable media (see interferences 3.1).

8.3 Use distilled water to set the transmittance at 100% and then determine the transmittance of the clarified sample or standard with each of the three tristimulus filters. Calibration standards from 25 to 250 units are recommended.

9. Calculations

9.1 Calculate intermediate tristimulus values for samples and standards from the transmittance data in 8.3 using the following equations:

$$X_s = (T_3 \times 0.1899) + (T_1 \times 0.791)$$

$$Y_s = T_2$$

$$Z_s = T_3 \times 1.1835$$

where:

T_1 = transmittance value in % using filter number 1

T_2 = transmittance value in % using filter number 2

T_3 = transmittance value in % using filter number 3

9.2 Convert tristimulus values to the corresponding Munsell values V_x, V_y and V_z by the use of published tables[2,3,4], or the equation suggested by Bridgeman[5].

9.3 Calculate DE values for samples and standards, construct a calibration curve by plotting DE against ADMI units of standards and determine ADMI color units of samples from the calibration curve.

$$DE = \sqrt{[0.23 \times (V_{yc} - V_{ys})]^2 + [(V_{xc} - V_{yc}) - (V_{xs} - V_{ys})]^2 + [0.4[(V_{yc} - V_{zc}) - (V_{ys} - V_{zs})]]^2}$$

where V_{xs}, V_{ys} and V_{zs} = the Munsell values for X_s, Y_s and Z_s respectively and V_{xc}, V_{yc} and V_{zc} = the Munsell values for a blank solution whose tristimulus values are X_c, Y_c and Z_c.

NOTE 1: If the photometer used is set at 100% transmittance with distilled water, the tristimulus values for the blank are 98.09, 100.00 and 118.35 for X_c, Y_c and Z_c respectively. If necessary, tristimulus values for the blank are determined as in calculation (9.1).

9.4 Report ADMI color values at pH 7.6 and at the original pH.

NOTE 2: The intermediate tristimulus values calculated under 9.1, using the three tristimulus filters, are used only to calculate the ADMI color value. They should not be reported as tristimulus values or used to determine dominant wavelength, luminance and purity.

10. Precision and Accuracy

10.1 Accuracy data on actual samples cannot be obtained.

10.2 Precision data are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition (1975), p 64.
2. J. Soc. Dyers and Colorists, 86, No. 8, 354 (1970).
3. Wyszecki and Stiles, Color Science, Wiley, N.Y., 1967, Tables 6.4 A, B and C.
4. Judd and Wyszecki, Color in Business, Science and Industry, 2nd Edition, Wiley, N.Y. (1963) Tables A, B and C in Appendix.
5. J. Opt. Soc. Am., Volume 53, page 499, April 1963.
6. Dyes and the Environment–Report on Selected Dyes and Their Effects, Volume 1, Sept. 1973 Appendix; American Dye Manufacturers Institute, Inc.

COLOR

Method 110.2 (Colorimetric-Platinum-Cobalt)

STORET NOS.
TRUE COLOR 00080
APPARENT COLOR 00081

1. Scope and Application
    1.1 The Platinum-Cobalt method is useful for measuring color of water derived from naturally occurring materials, i.e., vegetable residues such as leaves, barks, roots, humus and peat materials. The method is not applicable to color measurement on waters containing highly colored industrial wastes. See ADMI color method in this manual.

    NOTE 1: The Spectrophotometric and Tristimulus methods are useful for detecting specific color problems. The use of these methods, however, is laborious and unless determination of the hue, purity, and luminance is desired, they are of limited value.
2. Summary of Method
    2.1 Color is measured by visual comparison of the sample with platinum-cobalt standards. One unit of color is that produced by 1 mg/1 platinum in the form of the chloroplatinate ion.
3. Interferences
    3.1 Since very slight amounts of turbidity interfere with the determination, samples showing visible turbidity should be clarified by centrifugation.
    3.2 Method is pH dependent.
4. Sample Handling and Preservation
    4.1 Representative samples shall be taken in scrupulously clean glassware.
    4.2 Since biological activity may change the color characteristics of a sample, the determination should be made as soon as possible. Refrigeration at 4°C is recommended.
5. Apparatus
    5.1 Nessler tubes: Matched, tall form, 50 ml capacity.
6. Reagents
    6.1 Standard chloroplatinate solution: Dissolve 1.246 g potassium chloroplatinate, K_2PtCl_6, (equivalent to 0.500 g metallic Pt) and 1 g crystalline cobaltous chloride, $CoCl2 \bullet H_2O$, in distilled water containing 100 ml of conc. HCl. Dilute to 1000 ml with distilled water. This standard solution is equivalent to 500 color units.
7. Preparation of Standards
    7.1 Prepare standards in increments from 5 to 70 units. The following series is suggested:

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Ml of Standard Solution Diluted to 50.0 ml with Distilled Water	Color in Chloroplatinate Units
0.0	0
0.5	5
1.0	10
1.5	15
2.0	20
2.5	25
3.0	30
3.5	35
4.0	40
4.5	45
5.0	50
6.0	60
7.0	70

7.2 Protect these standards against evaporation and contamination by use of clean, inert stoppers.

NOTE 2: The standards also must be protected against the absorption of ammonia since an increase in color will result.

8. Procedure

8.1 Apparent color: Observe the color of the sample by filling a matched Nessler tube to the 50 ml mark with the water and compare with standards. This comparison is made by looking vertically downward through the tubes toward a white or specular surface placed at such an angle that light is reflected upward through the columns of liquid. If turbidity has not been removed by the procedure given in (8.2), report the color as "apparent color". If the color exceeds 70 units, dilute the sample with distilled water in known proportions until the color is within the range of the standards.

8.2 True color: Remove turbidity by centrifuging the sample until the supernatant is clear. The time required will depend upon the nature of the sample, the speed of the motor, and the radius of the centrifuge, but rarely will more than one hour be necessary. Compare the centrifuged sample with distilled water to insure that turbidity has been removed. If the sample is clear, then compare with standards as given in (8.1).

9. Calculation

9.1 Calculate the color units by means of the following equation:

$$\text{Color units} = \frac{A \times 50}{V}$$

where:

A = estimated color of diluted sample.
V = ml sample taken for dilution.

9.2 Report the results in whole numbers as follows:

Color Units	Record to Nearest
1–50	1
51–100	5
101–250	10
251–500	20

10. Precision and Accuracy

10.1 Precision and accuracy data are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 64, Method 204A (1975).

COLOR

Method 110.3 (Spectrophotometric)

STORET NO. 00080

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. It must be used for industrial wastes that cannot be determined by the Platinum-Cobalt method.
2. Summary of Method
   2.1 Color characteristics are measured at pH 7.6 and at the original pH by obtaining the visible absorption spectrum of the sample on a spectrophotometer. The percent transmission at certain selected wavelengths is used to calculate the results.
   2.2 The results are expressed in terms of dominant wavelength, hue, luminance, and purity.
3. Interferences
   3.1 Since very slight amounts of turbidity interfere with the determination, samples must be filtered before analysis.
4. Sample Handling and Preservation
   4.1 Since biological activity may change the color characteristics of a sample, the determination should be made as soon as possible. Refrigeration at 4°C is recommended.
5. Reference
   5.1 The procedure to be used for this determination is found in:
   Standard Methods for the Examination of Water and Wastewater, 14th Edition,
   p 66, Method 204B (1975).

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CONDUCTANCE

Method 120.1 (Specific Conductance, umhos at 25°C)

STORET NO. 00095

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline wates, domestic and industrial wastes and acid rain (atmospheric deposition).
2. Summary of Method
   2.1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.
   2.2 Samples are preferable analyzed at 25°C. If not, temprature corrections aremade and results reported at 25°C.
3. Comments
   3.1 Instrument must be standardized with KCl solution before daily use.
   3.2 Conductivity cell must be kept clean.
   3.3 Field measurements with comparable instruments are reliable.
   3.4 Temperature variations and corrections represent the largest source of potential error.
4. Sample Handling and Preservation
   4.1 Analyses can be performed either in the field or laboratory.
   4.2 If analysis is not completed within 24 hours of sample collection, sample should be filtered through a 0.45 micron filter and stored at 4°C. Filter and apparatus must be washed with high quality distilled water and pre-rinsed with sample before use.
5. Apparatus
   5.1 Conductivity bridge, range 1 to 1000 μmho per centimeter.
   5.2 Conductivity cell, cell constant 1.0 or micro dipping type cell with 1.0 constant. YSI #3403 or equivalent.
   5.4 Thermometer
6. Reagents
   6.1 Standard potassium chloride solutions, 0.01 M: Dissolve 0.7456 gm of pre-dried (2 hour at 105°C) KCl in distilled water and dilute to 1 liter at 25°C.
7. Cell Calibration
   7.1 The analyst should use the standard potassium chloride solution (6.1) and the table below to check the accuracy of the cell constant and conductivity bridge.

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Conductivity 0.01 m KCl

°C	Micromhos/cm
21	1305
22	1332
23	1359
24	1386
25	1413
26	1441
27	1468
28	1496

8. Procedure
   8.1 Follow the direction of the manufacturer for the operation of the instrument.
   8.2 Allow samples to come to room temperature (23 to 27°C), if possible.
   8.3 Determine the temperature of samples within 0.5°C. If the temperature of the samples is not 25°C, make temperature correction in accordance with the instruction in Section 9 to convert reading to 25°.
9. Calculation
   9.1 These temperature corrections are based on the standard KCl solution.
      9.1.1 If the temperature of the sample is below 25°C, add 2% of the reading per degree.
      9.1.2 If the temperature is above 25°C, subtract 2% of the reading per degree.
   9.2 Report results as Specific Conductance, µmhos/cm at 25°.
10. Precision and Accuracy
   10.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the following results:

Increment as Specific Conductance	Precision as Standard Deviation	Accuracy as	
		Bias, %	Bias, µmhos/cm
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1640	106	-5.36	-87.9
1710	119	-5.08	-86.9

(FWPCA Method Study 1, Mineral and Physical Analyses.)

   10.2 In a single laboratory (EMSL) using surface water samples with an average conductivity of 536 µmhos/cm at 25°C, the standard deviation was ±6.

Bibliography

1. The procedure to be used for this determination is found in: Annual Book of ASTM Standards Part 31, "Water," Standard D1125-64, p. 120 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 71, Method 205 (1975).
3. Instruction Manual for YSI Model 31 Conductivity Bridge.
4. Peden, M. E., and Skowron. "Ionic Stability of Precipitation Samples," Atmospheric Environment, Vol. 12, p. 2343-2344, 1978.

HARDNESS, Total (mg/1 as $CaCO_3$)

Method 130.1 (Colorimetric, Automated EDTA)

STORET NO. 00900

1. Scope and Application
   1.1 This automated method is applicable to drinking, surface, and saline waters. The applicable range is 10 to 400 mg/1 as $CaCO_3$. Approximately 12 samples per hour can be analyzed.
2. Summary of Method
   2.1 The magnesium EDTA exchanges magnesium on an equivalent basis for any calcium and/or other cations to form a more stable EDTA chelate than magnesium. The free magnesium reacts with calmagite at a pH of 10 to give a red-violet complex. Thus, by measuring only magnesium concentration in the final reaction stream, an accurate measurement of total hardness is possible.
3. Sample Handling and Preservation
   3.1 Cool to 4°C, HNO_3 to $pH < 2$.
4. Interferences
   4.1 No significant interferences.
5. Apparatus
   5.1 Technicon AutoAnalyzer consisting of:
      5.1.1 Sampler I.
      5.1.2 Continuous Filter.
      5.1.3 Manifold.
      5.1.4 Proportioning Pump.
      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters.
      5.1.6 Recorder equipped with range expander.
6. Reagents
   6.1 Buffer: Dissolve 67.6 g NH_4Cl in 572 ml of NH_4OH and dilute to 1 liter with distilled water.
   6.2 Calmagite Indicator: Dissolve 0.25 g in 500 ml of distilled water by stirring approximately 30 minutes on a magnetic stirrer. Filter.
   6.3 Monomagnesium ethylenediamine-tetraacetate (MgEDTA): Dissolve 0.2 g of MgEDTA in 1 liter of distilled water.
   6.4 Stock Solution: Weigh 1.000 g of calcium carbonate (pre-dried at 105°C) into 500 ml Erlenmeyer flask; add 1:1 HCl until all $CaCO_3$ has dissolved. Add 200 ml of distilled water and boil for a few minutes. Cool, add a few drops of methyl red indicator, and adjust to the orange color with 3N NH_4OH and dilute to 1000 ml with distilled water. 1.0 ml = 1.0 mg $CaCO_3$.

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6.4.1 Dilute each of the following volumes of stock solutions to 250 ml in a volumetric flask for appropriate standards:

Stock Solution, ml	$CaCO_3$, mg/l
2.5	10.0
5.0	20.0
10.0	40.0
15.0	60.0
25.0	100.0
35.0	140.0
50.0	200.0
75.0	300.0
100.0	400.0

6.5 Ammonium Hydroxide, 1N: Dilute 70 ml of conc. NH_4OH to 1 liter with distilled water.

7. Procedure

7.1 Pretreatment

7.1.1 For drinking waters, surface waters, saline waters, and dilutions thereof, no pretreatment steps are necessary. Proceed to 7.2.

7.1.2 For most wastewaters, and highly polluted waters, the sample must be digested as given in the Atomic Absorption Methods section of this manual, paragraphs 4.1.3 and 4.1.4. Following this digestion, proceed to 7.2.

7.2 Neutralize 50.0 ml of sample with 1N ammonium hydroxide (6.5) and note volume of NH_4OH used.

7.3 Set up manifold as shown in Figure 1.

7.4 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.5 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.5 minutes.

7.6 Arrange working standards in Sampler in order of decreasing concentrations. Complete loading of Sampler tray with unknown samples.

7.7 Switch sample line from distilled water to Sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve. Correct for amount of NH_4OH used in 7.2 as follows:

$$\text{mg/l} = \frac{A}{50} \times B$$

where:

A = Vol. of sample plus volume of NH_4OH
B = Concentration from standard curve

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 19, 120, 385, and 366 mg/1 as $CaCO_3$, the standard deviations were ±1.5, ±1.5, ±4.5, and ±5.0, respectively.

9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 39 and 296 mg/1 as $CaCO_3$, recoveries were 89% and 93%, respectively.

Bibliography

1. Technicon AutoAnalyzer Methodology, Bulletin No. 2, Technicon Controls, Inc., Chauncey, New York (July 1960).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 202, Method 309B (1975).

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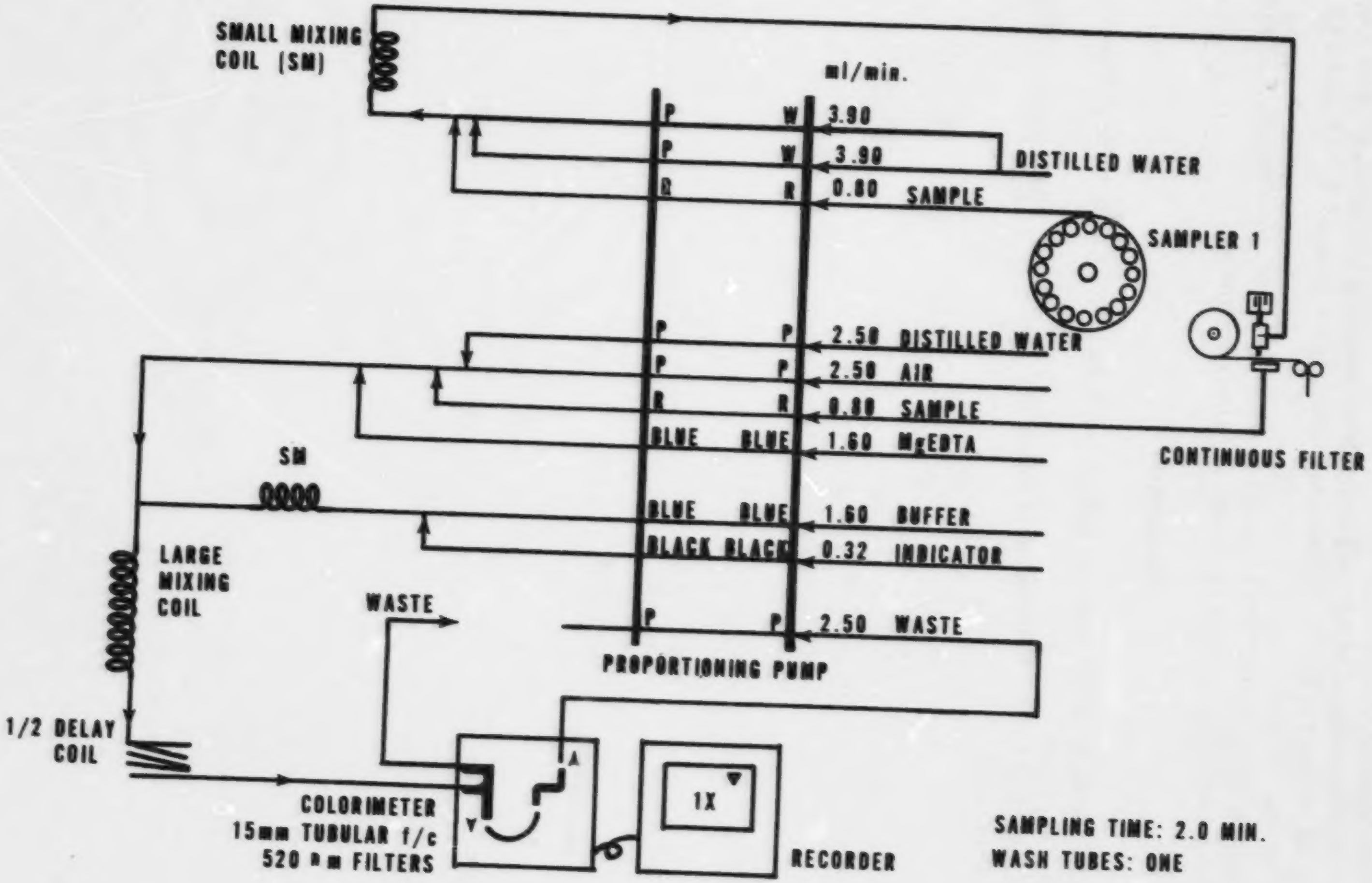
SMALL MIXING COIL (SM)
ml/min.
P
W
3.90
P
W
3.90
DISTILLED WATER
R
R
0.80
SAMPLE
SAMPLER 1
P
P
2.50
DISTILLED WATER
P
P
2.50
AIR
R
R
0.80
SAMPLE
BLUE
BLUE
1.60
MgEDTA
CONTINUOUS FILTER
SM
BLUE
BLUE
1.60
BUFFER
BLACK
BLACK
0.32
INDICATOR
LARGE MIXING COIL
WASTE
P
P
2.50
WASTE
PROPORTIONING PUMP
1/2 DELAY COIL
1X
COLORIMETER
15mm TUBULAR f/c
520 nm FILTERS
RECORDER
SAMPLING TIME: 2.0 MIN.
WASH TUBES: ONE

FIGURE 1. HARDNESS MANIFOLD AA-I

HARDNESS, Total (mg/1 as $CaCO_3$)
Method 130.2 (Titrimetric, EDTA)

STORET NO. 00900

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The method is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25 mg $CaCO_3$.
   - 1.3 Automated titration may be used.
2. Summary of Method
   - 2.1 Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction is detected by means of Eriochrome Black T indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.
3. Sample Handling and Preservation
   - 3.1 Cool to 4°C, HNO_3 to $pH < 2$.
4. Comments
   - 4.1 Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with cyanide.
     - 4.1.1 Routine addition of sodium cyanide solution (Caution: deadly poison) to prevent potential metallic interference is recommended.
5. Apparatus
   - 5.1 Standard laboratory titrimetric equipment.
6. Reagents
   - 6.1 Buffer solution
     - 6.1.1 If magnesium EDTA is available: Dissolve; 16.9 g NH_4C1 in 143 m1 conc. NH_4OH in a 250 m1 volumetric, add 1.25 g of magnesium salt of EDTA and dilute to the mark with distilled water. Then go to 6.1.3.
     - 6.1.2 If magnesium EDTA is unavailable: Dissolve 1.179 g disodium EDTA (analytical reagent grade) and 780 mg $MgSO_4 \cdot 7H_2O$ (or 644 mg $MgCl_2 \cdot 6H_2O$) in 50 ml distilled water. Add this solution to a 250 m1 volumetric flask containing 16.9 g NH_4C1 and 143 m1 conc. NH_4OH with mixing and dilute to the mark with distilled water.
     - 6.1.3 Store in a tightly stoppered plastic bottle; stable for approximately one month. Dispense with bulb operated pipet. Discard when 1 or 2 m1 added to sample fails to produce a pH of 10.0 ±0.1 at end point of titration.

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6.1.4 Commercially available "odorless buffers" which are more stable, may be used.

6.2 Inhibitors: For most waters inhibitors are not necessary. If interfering ions are present use one of the following:

6.2.1 Inhibitor I: NaCN powder. (Caution: extremely poisonous). Flush solutions or sample containing this down drain using large quantities of water. Make sure no acids are present which might liberate HCN gas.

6.2.2 Inhibitor II: Dissolve 5.0 g $Na_2S{\cdot}9\ H_2O$ or 3.7 g $Na_2S{\cdot}5\ H_2O$ in 100 m1 distilled water. Exclude air with tightly fitted rubber stopper. This gives sulfide precipitates which may obscure the end point if large quantities of heavy metals are present. Deteriorates rapidly through air oxidation.

6.2.3 Inhibitor III: Dissolve 4.5 g hydroxylamine hydrochloride in 100 ml of 95% ethanol or isopropanol.

6.3 Indicator: Use a commercially available indicator such as Calmagite indicator (Mallinckrodt) or one of the formulations described below (6.3.1–6.3.3)

6.3.1 Mix 0.5 g Eriochrome Black T with 4.5 g hydroxylamine hydrochloride. Dissolve in 100 m1 of 95% ethanol or isopropanol.

6.3.2 Dissolve 0.5 to 1.0 g Eriochrome Black T in an appropriate solvent such as triethanolamine or 2-methoxyethanol. Stable approximately one week.

6.3.3 Mix together 0.5 g Eriochrome Black T and 100 g NaC1.

6.4 Standard EDTA titrant, 0.02 N: Place 3.723 g analytical reagent grade disodium ethylenediamine tetraacetate dihydrate, $Na_2H_2C_{10}H_{12}O_8N_2{\cdot}2\ H_2O$ in a 1 liter volumetric flask and dilute to the mark with distilled water. Check with standard calcium solution (6.4.1) by titration (6.4.5). Store in polyethylene. Check periodically because of gradual deterioration.

6.4.1 Standard calcium solution 0.02 N: Place 1.000 g anhydrous calcium carbonate (primary standard low in metals) in a 500 ml flask. Add, a little at a time, 1 + 1 HCL (6.4.2) until all of the $CaCO_3$ has dissolved. Add 200 ml distilled water. Boil for a few minutes to expel CO_2. Cool. Add a few drops of methyl red indicator (6.4.3) and adjust to intermediate orange color by adding 3N NH_4OH (6.4.4) or 1 + 1 HCl (6.4.2) as required. Quantitatively transfer to a 1 liter volumetric flask and dilute to mark with distilled water.

6.4.2 Hydrochloric acid solution, 1 + 1.

6.4.3 Methyl red indicator: Dissolve 0.10 g methyl red in distilled water in a 100 ml volumetric flask and dilute to the mark.

6.4.4 Ammonium hydroxide solution, 3 N: Dilute 210 ml of conc. NH_4OH to 1 liter with distilled water.

6.4.5 Standardization titration procedure: Place 10.0 ml standard calcium solution (6.4.1) in vessel containing about 50 m1 distilled water. Add 1 m1 buffer solution (6.1). Add 1–2 drops indicator (6.3) or small scoop of dry indicator (6.3.3). Titrate slowly with continuous stirring until the last reddish tinge disappears, adding last few drops at 3–5 second intervals. At end point the color is blue. Total titration duration should be 5 minutes from the time of buffer addition.

$$\text{N of EDTA} = \frac{0.2}{\text{ml of EDTA}}$$

6.5 Ammonium Hydroxide, 1N: Dilute 70 ml of conc. NH_4OH to 1 liter with distilled water.

7. Procedure

7.1 Pretreatment

7.1.1 For drinking waters, surface waters, saline waters, and dilutions thereof, no pretreatment steps are necessary. Proceed to 7.2.

7.1.2 For most wastewaters, and highly polluted waters, the sample must be digested as given in the Atomic Absorption Methods section of this manual, paragraphs 4.1.3 and 4.1.4. Following this digestion, proceed to 7.2.

7.2 Titration of sample-normal to high hardness:

7.2.1 Sample should require < 15 ml EDTA titrant (6.4) and titration should be completed within 5 minutes of buffer addition.

7.2.2 Place 25.0 ml sample in titration vessels, neutralize with 1N ammonium hydroxide (6.5) and dilute to about 50 ml.

7.2.3 Add 1 to 2 ml buffer solution (6.1).

7.2.4 If end point is not sharp (as determined by practice run) add inhibitor at this point (see 7.4).

7.2.5 Add 1 to 2 drops indicator solution (6.3.1 or 6.3.2) or small scoop of dried powder indicator formulation (6.3.3).

7.2.6 Titrate slowly with continuous stirring with standard EDTA titrant (6.4) until last reddish tint disappears. Solution is normally blue at end point.

7.3 Titration of sample–low hardness (less than 5 mg/1)

7.3.1 Use a larger sample (100 ml)

7.3.2 Use proportionately larger amounts of buffer, inhibitor and indicator

7.3.3 Use a microburet and run a blank using redistilled, distilled or deionized water.

7.4 To correct for interferences:

7.4.1 Some metal ions interfere by causing fading or indistinct end points. Inhibitors reduce this in accord with the scheme below for 25.0 ml samples diluted to 50 ml.

Maximum Concentrations of Interferences Permissible with Various Inhibitors[a]

Interfering Substance	Maximum Interference Concentration mg/l		
	Inhibitor I	Inhibitor II	Inhibitor III
Aluminum	20	20	20
Barium	b	b	b
Cadmium	b	20	b
Cobalt	over 20	0.3	0[c]
Copper	over 30	20	0.3
Iron	over 30	5	20
Lead	b	20	b
Manganese (Mn^{2+})	b	1	1
Nickel	over 20	0.3	0[c]
Strontium	b	b	b
Zinc	b	200	b
Polyphosphate		10	

a Based on 25-ml sample diluted to 50 ml.
b Titrates as hardness.
c Inhibitor fails if substance is present.

7.4.2 Inhibitor I: At step 7.2.4 add 250 mg NaCN. Add sufficient buffer to achieve pH 10.0 ± 0.1 to offset alkalinity resulting from hydrolysis of sodium cyanide.

7.4.3 Inhibitor II: At step 7.2.4 add 1 ml of inhibitor II (6.2.2)

7.4.4 Inhibitor III: At step 7.2.4 add 1 ml of inhibitor III (6.2.3).

8. **Calculations:**

$$\text{Hardness (EDTA) mg } CaCO^3/l = \frac{A \times N \times 50{,}000}{\text{ml sample}}$$

where:
A = ml EDTA titrant (6.4)
N = normality of EDTA titrant.

9. Precision and Accuracy

9.1 Forty-three analysts in nineteen laboratories analyzed six synthetic water samples containing exact increments of calcium and magnesium salts, with the following results:

Increment as Total Hardness mg/liter, $CaCO_3$	Precision as Standard Deviation mg/liter, $CaCO_3$	Accuracy as Bias, %	Accuracy as Bias, mg/liter, $CaCO_3$
31	2.87	–0.87	–0.003
33	2.52	–0.73	–0.24
182	4.87	–0.19	–0.4
194	2.98	–1.04	–2.0
417	9.65	–3.35	–13.0
444	9.73	–3.23	–14.3

(FWPCA Method Study 1, Mineral and Physical Analyses)

9.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 194 mg $CaCO_3$/1, the standard deviation was ±3.

9.3 A synthetic unknown sample containing 610 mg/1 total hardness as $CaCO_3$ contributed by 108 mg/1 Ca and 82 mg/1 Mg, and the following supplementary substances: 3.1 mg/1 K, 19.9 mg/1 Na, 241 mg/1 chloride, 0.25 mg/1 nitrite N, 1.1 mg/1 nitrate N, 259 mg/1 sulfate, and 42.5 mg/1 total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 56 laboratories by the EDTA titrimetric method with a relative standard deviation of 2.9% and a relative error of 0.8%.

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ODOR

Method 140.1 (Threshold Odor, Consistent Series)

STORET NO. 60°C: 00086
Room Temp: 00085

1. Scope and Application
   1.1 This method is applicable to the determination of threshold odor of drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 Highly odorous samples are reduced in concentration proportionately before being tested. Thus, the method is applicable to samples ranging from nearly odorless natural waters to industrial wastes with threshold odor numbers in the thousands.
2. Summary of Method(1)
   2.1 The sample of water is diluted with odor-free water until a dilution that is of the least definitely perceptible odor to each tester is found. The resulting ratio by which the sample has been diluted is called the "threshold odor number" (T.O.N.).
   2.2 People vary widely as to odor sensitivity, and even the same person will not be consistent in the concentrations they can detect from day to day. Therefore, panels of not less than five persons, and preferably 10 or more, are recommended to overcome the variability of using one observer.(2) As an absolute minimum, two persons are necessary: One to make the sample dilutions and one to determine the threshold odor.
3. Sample Handling and Preservation
   3.1 Water samples must be collected in glass bottles with glass or Teflon-lined closures. Plastic containers are not reliable for odor samples and must not be used.
   3.2 Odor tests should be completed as soon as possible after collection of the sample. If storage is necessary, collect at least 1000 ml of sample in a bottle filled to the top. Refrigerate, making sure no extraneous odors can be drawn into the sample as the water cools.
4. Interferences
   4.1 Most tap waters and some waste waters are chlorinated. It is often desirable to determine the odor of the chlorinated sample as well as of the same sample after removal of chlorine. Dechlorination is achieved using sodium thiosulfate in exact stoichiometric quantity.
      4.1.1 It is important to check a blank to which a similar amount of dechlorinating agent has been added to determine if any odor has been imparted. Such odor usually disappears upon standing if excess reagent has not been added.
5. Apparatus
   5.1 Odor-free glassware: Glassware must be freshly cleaned shortly before use, with non-odorous soap and acid cleaning solution followed by rinsing with odor-free water (6.1).

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Glassware used in odor testing should be reserved for that purpose only. Rubber, cork, and plastic stoppers must not be used.

5.2 Constant temperature bath: A water bath or electric hotplate capable of maintaining a temperature control of ±1°C for performing the odor test at 60°C. The temperature bath must not contribute any odor to the odor flasks.

5.3 Odor flasks: Glass stoppered 500 ml (₸ 32) Erlenmeyer flasks, or wide-mouthed 500 ml Erlenmeyer flasks equipped with Petri dishes as cover plates.

NOTE: Narrow-mouth vessels are not suitable for running odor tests. Potential positive bias due to color and/or turbidity of water sample under observation can be eliminated by wrapping odor flasks in aluminum foil, painting flasks with non-odorous paint, or by using red actinic Erlenmeyer flasks.

5.4 Sample bottles: Glass bottles with glass or Teflon-lined closures.

5.5 Pipets, measuring: 10.0 and 1.0 ml graduated in tenths.

5.6 Graduated cylinders: 250, 200, 100, 50, and 25 ml.

5.7 Thermometer: 0–110°C (±1°C), chemical or metal stem dial type.

5.8 Odor-free water generator: See Figure 1.

6. Reagents

6.1 Odor-free water: Odor-free dilution water must be prepared as needed by filtration through a bed of activated carbon. Most tap waters are suitable for preparation of odor-free waters, except that it is necessary to check the filtered water for chlorine residual, unusual salt concentrations, or unusually high or low pH. All these may affect some odorous samples.

Where supplies are adequate, distilled water avoids these problems as a source of odor-free water. A convenient odor-free water generator may be made as shown in Figure 1. Pass tap or distilled water through the odor-free water generator at a rate of 0.1 liter/minute. When the generator is first started, it should be flushed to remove carbon fines before the odor-free water is used.

6.1.1 The quality of water obtained from the odor-free water generator should be checked daily at the temperature tests are to be conducted (room temperature and/or 60°C). The life of the carbon will vary with the condition and amount of water filtered. Subtle odors of biological origin are often found if moist carbon filters are permitted to stand idle between test periods. Detection of odor in the water coming through the carbon indicates a change of carbon is needed.

7. Procedure

7.1 Precaution: Selection of persons to make odor tests should be carefully made. Extreme sensitivity is not required, but insensitive persons should not be used. A good observer has a sincere interest in the test. Extraneous odor stimuli such as those caused by smoking and eating prior to the test or through the use of scented soaps, perfumes, and shaving lotions must be avoided. The tester should be free from colds or allergies that affect odor-response. Frequent rests in an odor-free atmosphere are recommended. The room in which the tests are to be conducted should be free from distractions, drafts, and other odor. In certain industrial atmospheres, a special odor-free room may be required, ventilated by air filtered through activated carbon and maintained at a constant comfortable temperature and humidity. For precise work a panel of five or more testers should be used. The persons making the odor measurements should not prepare the samples and should not know the dilution concentrations being evaluated. These persons should have been made familiar with the procedure before participating in a panel test. Always start with the most dilute sample to avoid tiring the senses with the concentrated sample. The temperature of the samples during testing should be kept within 1 degree of the specified temperature for the test.

7.2 Threshold measurement: The ratio by which the odor-bearing sample has to be diluted with odor-free water for the odor to be just detectable by the odor test is the "threshold odor number" (T.O.N.). The total volume of sample and odor-free water used in each test is 200 ml. The proper volume of odor-free water is put into the flask first; the sample is then added to the water. Table 1 gives the dilutions and corresponding threshold numbers.

Table 1

Threshold Odor Number
Corresponding to Various Dilutions

Sample Volume (ml) Diluted to 200 ml	Threshold Odor Number
200	1
100	2
50	4
25	8
12.5	16
6.3	32
3.1	64
1.6	128
0.8	256

7.3 Determine the approximate range of the threshold odor by:

7.3.1 Adding 200 ml, 50 ml, 12.5 ml, and 3.1 ml of the sample to separate 500 ml glass-stoppered Erlenmeyer flasks containing odor-free water to make a total volume of 200 ml. A separate flask containing only odor-free water serves as the reference for comparison. If run at 60°C, heat the dilutions and the reference in the constant temperature bath at 60°C (±1°C).

7.3.2 Shake the flask containing the odor-free water, remove the stopper, and sniff the vapors. Test the sample containing the least amount of odor-bearing water in the same way. If odor can be detected in this dilution, more dilute samples must be prepared as described in (7.3.3). If odor cannot be detected in the first dilution, repeat the above procedure using the sample containing the next higher concentration of the odor-bearing water, and continue this process until odor is clearly detected.

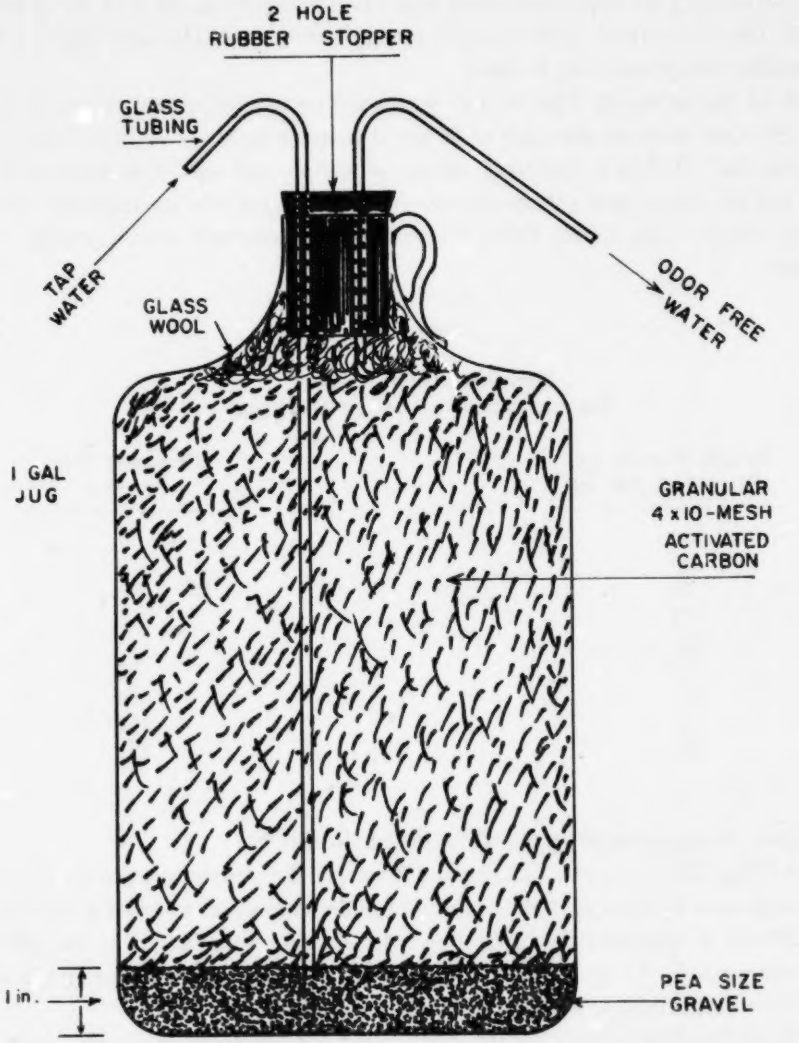
2 HOLE
RUBBER STOPPER
GLASS TUBING
TAP WATER
GLASS WOOL
ODOR FREE WATER
1 GAL JUG
GRANULAR 4 x 10-MESH ACTIVATED CARBON
1 in.
PEA SIZE GRAVEL

FIGURE 1. ODOR-FREE WATER GENERATOR

7.3.3 If the sample being tested requires more extensive dilution than is provided by Table 1, an intermediate dilution is prepared from 20 ml of sample diluted to 200 ml with odor-free water. Use this dilution for the threshold determination. Multiply the T.O.N. obtained by ten to correct for the intermediate dilution. In rare cases more than one tenfold intermediate dilution step may be required.

7.4 Based on the results obtained in the preliminary test, prepare a set of dilutions using Table 2 as a guide. One or more blanks are inserted in the series, in the vicinity of the expected threshold, but avoiding any repeated pattern. The observer does not know which dilutions are odorous and which are blanks. He smells each flask in sequence, beginning with the least concentrated sample and comparing with a known flask of odor-free water, until odor is detected with utmost certainty.

Table 2
Dilutions for Various Odor Intensities

Sample Volume in Which Odor First Noted			
200 ml	50 ml	12.5 ml	3.1 ml
Volume (ml) of Sample to be Diluted to 200 ml			
200	100	50	(intermediate Dilution See 7.3.3)
100	50	25	
50	25	12.5	
25	12.5	6.3	
12.5	6.3	3.1	

7.5 Record the observations of each tester by indicating whether odor is noted (+ sign) in each test flask.

For example:

ml sample diluted to 200 ml	12.5	0	25	0	50	100	200
Response	–	–	+	–	+	+	+

8. Calculations

8.1 The threshold odor number is the dilution ratio at which odor is just detectable. In the example above (7.5), the first detectable odor occurred when 25 ml sample was diluted to 200 ml. Thus, the threshold is 200 divided by 25, equals 8. Table 1 lists the threshold odor numbers that correspond to common dilutions.

8.2 Anomalous responses sometimes occur; a low concentration may be called positive and a higher concentration in the series may be called negative. In such a case, the threshold is designated as that point of detection after which no further anomalies occur.

For instance:

ml sample diluted to 200 ml	6.3	12.5	0	25	50	100
Response threshold	+	–	–	+	+	+
				↑ Threshold		

8.3 Calculations of panel results to find the most probable average threshold are best accomplished by appropriate statistical methods. For most purposes, the threshold of a group can be expressed as the geometric mean of the individual thresholds. The geometric mean is calculated in the following manner:

8.3.1 Obtain odor response as outlined in Procedure and record results.

For example:

Table 3
Sample Odor Series

ml of Odor-free water	ml of Sample	Observer Response*				
		1	2	3	4	5
188	12.5	–	–	–	–	–
175	25	–	⊕	–	+	⊕
200	0	–	–	–	–	–
150	50	⊕	+	–	–	+
200	0	–	–	–	–	–
100	100	+	+	⊕	⊕	+
0	200	+	+	+	+	+

*Circled plus equals threshold level.

8.3.2 Obtain individual threshold odor numbers from Table 1.

Observer	T.O.N.
1	4
2	8
3	2
4	2
5	8

8.3.3 The geometric mean is equal to the nth root of the product of n numbers. Therefore:

$$4 \times 8 \times 2 \times 2 \times 8 = 1{,}024$$

and $\sqrt[5]{1{,}024} = \dfrac{\log 1{,}024}{5} = \dfrac{3.0103}{5} = 0.6021$

and anti-log of 0.6021 = 4 = T.O.N.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

9.2 A threshold number is not a precise value. In the case of the single observer, it represents a judgment at the time of testing. Panel results are more meaningful because individual differences have less influence on the result. One or two observers can develop useful data if comparison with larger panels has been made to check their sensitivity. Comparisons of data from time to time or place to place should not be attempted unless all test conditions have been carefully standardized and some basis for comparison of observer intensities exists.

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1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 75, Method 206, (1975).
2. ASTM, Comm E-18, STP 433, "Basic Principles of Sensory Evaluation"; STP 434, Manual on Sensory Testing Methods; STP 440, "Correlation of Subjective-Objective Methods in the Study of Odors and Taste"; Phil., Pennsylvania (1968).
3. Baker, R. A., "Critical Evaluation of Olfactory Measurement". Jour. WPCF, 34, 582 (1962).

pH

Method 150.1 (Electrometric)

STORET NO.
Determined on site 00400
Laboratory 00403

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition).
2. Summary of Method
   2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.
3. Sample Handling and Preservation
   3.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.
   3.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.
4. Interferences
   4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
   4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.
   4.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1 + 9) may be necessary to remove any remaining film.
   4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.
5. Apparatus
   5.1 pH Meter-laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

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5.2 Glass electrode.

5.3 Reference electrode–a calomel, silver-silver chloride or other reference electrode of constant potential may be used.

NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel type filling materials that require minimal maintenance.

5.4 Magnetic stirrer and Teflon-coated stirring bar.

5.5 Thermometer or temperature sensor for automatic compensation.

6. Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is necessary.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.

7. Calibration

7.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart.

7.2.1 Various instrument designs may involve use of a "balance" or "standardize" dial and/or a slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until readings are within 0.05 pH units of the buffer solution value.

8. Procedure

8.1 Standardize the meter and electrode system as outlined in Section 7.

8.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar.

8.2.1 If field measurements are being made the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movement across the electrode sensing element as indicated by drift free (<0.1 pH) readings.

8.3 If the sample temperature differs by more than 2°C from the buffer solution the measured pH values must be corrected. Instruments are equipped with automatic or manual

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(1) National Bureau of Standards Special Publication 260.

compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

8.4 After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.

8.5 For acid rain samples it is most important that the magnetic stirrer is not used. Instead, swirl the sample gently for a few seconds after the introduction of the electrode(s). Allow the electrode(s) to equilibrate. The air-water interface should not be disturbed while measurement is being made. If the sample is not in equilibrium with the atmosphere, pH values will change as the dissolved gases are either absorbed or desorbed. Record sample pH and temperature.

9. Calculation

9.1 pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest °C.

10. Precision and Accuracy

10.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as Bias, %	Accuracy as Bias, pH Units
3.5	0.10	–0.29	–0.01
3.5	0.11	–0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	–0.03	–0.002
8.0	0.13	–0.12	–0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

10.2 In a single laboratory (EMSL), using surface water samples at an average pH of 7.7, the standard deviation was ±0.1.

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1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 460, (1975).
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United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

pH, Continuous Monitoring (Electrometric)—Method 150.2

1. Scope and Application

1.1 This method is applicable to the continuous pH measurement of drinking, surface, and saline waters, domestic and industrial waste waters.

2. Summary of Method

2.1 The pH of a sample is determined electrometrically using a glass electrode with a reference electrode or a single combination electrode.

3. Sample Handling and Preservation

3.1 The composition of the water or waste contacting the measuring electrode system must be representative of the total flow from the water body.

4. Interferences

4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.

4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.

4.3 Manually inspect the conditions of the electrodes every 30 days for coating by oily materials or buildup of lime. If oil and grease and/or scale buildup are not present, this time interval may be extended.

4.3.1 Coatings of oil, grease and very fine solids can impair electrode response. These can usually be removed by gentle wiping and detergent washing. The use of flow-through electrode housings which provide higher flow velocity helps to prevent the coating action.

4.3.2 Heavy particulate matter such as lime accumulation can be removed by careful scrubbing or immersion in dilute (1+9) hydrochloric acid. Continuous monitoring under these conditions benefits from ultrasonic or other in-line continuous cleaning methods.

4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. For best results, meters having automatic temperature compensation should be calibrated with solutions within 5°C of the temperature of the stream to be measured. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.

5. Apparatus

5.1 pH Monitor - A wide variety of instruments are commercially available with various specifications and optional equipment. For unattended use, the monitor should be equipped with automatic or fixed temperature compensation and with a recorder or alarm function.

5.2 Glass electrode - with shielded cable between electrode and monitor unless preamplification is used.

5.3 Reference electrode - a reference electrode with a constant potential and with either a visible electrolyte or viscous gel fill.
NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

5.4 Temperature sensor - for automatic compensator covering general ambient temperature range.

5.5 Electrode mounting - to hold electrodes; may be flow through (for small flows), pipe mounted or immersion.

6. Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is required.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, which have been validated by comparison to NBS standards, is recommended for routine operation. These buffers may be retained for at least six months if kept stoppered.

7. Calibration

7.1 Immersion type electrodes - easily removed from mounting.

7.1.1 The electrode should be calibrated at a minimum of two points that bracket the expected pH of the water/waste and are approximately three pH units or more apart.

7.1.2 Repeat calibration adjustments on successive portions of the two buffer solutions until readings are within ±0.05 pH units of the buffer value. If calibration problems occur, see 4.3.

7.1.3 Because of the wide variety of instruments available, no detailed operating instructions are provided. Instead, the analyst should refer to the particular manufacturer's instructions.

7.1.4 Calibration against two buffers should be carried out at least daily. If the pH of the fluid being measured fluctuates considerably, the calibration should be carried out more often. Calibration frequencies may be relaxed if historical data supports a longer period between calibration.

7.2 Immersion type electrodes - not easily removed from mounting.

7.2.1 Collect a grab sample of the flowing material from a point as close to the electrode as possible. Measure the pH of this grab sample as quickly as possible with a laboratory - type pH meter. Adjust the calibration control of the continuous monitor to the reading obtained.

7.2.2 The temperature and condition of the grab sample must remain constant until its pH has been measured by the laboratory pH meter. The temperature of the sample should be measured and the temperature compensator of the laboratory pH meter adjusted.

7.2.3 The laboratory - type pH meter should be calibrated prior to use against two buffers as outlined in 7.1.

7.2.4 The continuous pH monitoring system should be initially calibrated against two buffers as outlined in 7.1 before being placed into service. Recalibration (every 30 days) at two points is recommended if at all possible to ensure the measuring electrode is in working order. If this is not possible, the use of electrode testing features for a broken or malfunctioning electrode should be considered when purchasing the equipment.

7.2.5 The indirect calibration should be carried out at least once a day. If the pH of the fluid being measured fluctuates considerably, the calibration should be carried out more often. Calibration frequencies may be relaxed if historical data support a longer period between calibration.

7.2.6 If the electrode can be removed from the system, but with difficulty, it should be directly calibrated as in 7.1 at least once a month.

7.3 Flow-through type electrode - easily removed from its mounting.

7.3.1 Calibrate using buffers as in 7.1. The buffers to be used may be the process stream itself as one buffer, and as a second buffer after adjustment of pH by addition of an acid or base. This will provide the larger volumes necessary to calibrate this type electrode.

7.3.2 Since the velocity of sample flow-through a flow through electrode can produce an offset error in pH reading, the user must have data on hand to show that the offset is known and compensation has been accomplished.

7.4 Flow-through type electrode - not easily removed from its mounting.

7.4.1 Calibrate as in 7.2.

7.4.2 Quality control data must be on hand to show the user is aware of possible sample flow velocity effects.

8. Procedure

8.1 Calibrate the monitor and electrode system as outlined in Section 7.

8.2 Follow the manufacturer's recommendation for operation and installation of the system.

8.3 In wastewaters, the electrode may require periodic cleaning. After manual cleaning, the electrode should be calibrated as in 7.1 or 7.2 before returning to service.

8.4 The electrode must be placed so that the water or waste flowing past the electrode is representative of the system.

9. Calculations

9.1 pH meters read directly in pH units. Reports pH to the nearest 0.1 unit and temperature to the nearest °C.

10. Precision and Accuracy

10.1 Because of the wide variability of equipment and conditions and the changeable character of the pH of many process waters and wastes, the precision of this method is probably less than that of Method 150.1; however, a precision of 0.1 pH unit

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[1] National Bureau of Standards Special Publication 260.

should be attainable in the range of pH 6.0 to 8.0. Accuracy data for continuous monitoring equipment are not available at this time.

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1. Annual Book of ASTM Standards, Part 31, "Water" Standard 1293-78, Method D, p. 226 (1981).

RESIDUE, FILTERABLE

Method 160.1 (Gravimetric, Dried at 180°C)

STORET NO. 70300

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The practical range of the determination is 10 mg/1 to 20,000 mg/1.
2. Summary of Method
   - 2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.
   - 2.2 If Residue, Non-Filterable is being determined, the filtrate from that method may be used for Residue, Filterable.
3. Definitions
   - 3.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.
4. Sample Handling and Preservation
   - 4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   - 5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.
   - 5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.
   - 5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.
6. Apparatus
   - 6.1 Glass fiber filter discs, 4.7 cm or 2.1 cm, without organic binder, Reeve Angel type 934-AH, Gelman type A/E, or equivalent.
   - 6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.
   - 6.3 Suction flask, 500 ml.
   - 6.4 Gooch crucibles, 25 ml (if 2.1 cm filter is used).
   - 6.5 Evaporating dishes, porcelain, 100 ml volume. (Vycor or platinum dishes may be substituted).
   - 6.6 Steam bath.
   - 6.7 Drying oven, 180°C ±2°C.
   - 6.8 Desiccator.

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6.9 Analytical balance, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.

7.2 Preparation of evaporating dishes: If Volatile Residue is also to be measured heat the clean dish to 550 ±50°C for one hour in a muffle furnace. If only Filterable Residue is to be measured heat the clean dish to 180 ±2°C for one hour. Cool in desiccator and store until needed. Weigh immediately before use.

7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml graduated cylinder. If total filterable residue is low, a larger volume may be filtered.

7.4 Filter the sample through the glass fiber filter, rinse with three 10 ml portions of distilled water and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

7.5 Transfer 100 ml (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.

7.6 Dry the evaporated sample for at least one hour at 180 ±2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

8. Calculation

8.1 Calculate filterable residue as follows:

$$\text{Filterable residue, mg/1} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of dried residue + dish in mg
B = weight of dish in mg
C = volume of sample used in ml

9. Precision and Accuracy

9.1 Precision and accuracy are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 92, Method 208B, (1975).

RESIDUE, NON-FILTERABLE

Method 160.2 (Gravimetric, Dried at 103–105°C)

STORET NO. 00530

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The practical range of the determination is 4 mg/1 to 20,000 mg/1.
2. Summary of Method
   - 2.1 A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103–105°C.
   - 2.2 The filtrate from this method may be used for Residue, Filterable.
3. Definitions
   - 3.1 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103–105°C.
4. Sample Handling and Preservation
   - 4.1 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
   - 4.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   - 5.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.
   - 5.2 Samples high in Filterable Residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter (7.5) minimizes this potential interference.
6. Apparatus
   - 6.1 Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.

     NOTE: Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as "pore size", collection efficiencies and effective retention are used to define this property in glass fiber filters. Values for these parameters vary for the filters listed above.
   - 6.2 Filter support: filtering apparatus with reservoir and a coarse (40–60 microns) fritted disc as a filter support.

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NOTE: Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch or Buchner funnels, membrane filter holders and Gooch crucibles. All are available with coarse fritted disc.

6.3 Suction flask.

6.4 Drying oven, 103–105°C.

6.5 Desiccator.

6.6 Analytical balance, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the glass fiber filter on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103–105°C for one hour. Remove to desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only.

7.2 Selection of Sample Volume

For a 4.7 cm diameter filter, filter 100 ml of sample. If weight of captured residue is less than 1.0 mg, the sample volume must be increased to provide at least 1.0 mg of residue. If other filter diameters are used, start with a sample volume equal to 7 ml/cm^2 of filter area and collect at least a weight of residue proportional to the 1.0 mg stated above.

NOTE: If during filtration of this initial volume the filtration rate drops rapidly, or if filtration time exceeds 5 to 10 minutes, the following scheme is recommended: Use an unweighed glass fiber filter of choice affixed in the filter assembly. Add a known volume of sample to the filter funnel and record the time elapsed after selected volumes have passed through the filter. Twenty-five ml increments for timing are suggested. Continue to record the time and volume increments until fitration rate drops rapidly. Add additional sample if the filter funnel volume is inadequate to reach a reduced rate. Plot the observed time versus volume filtered. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.

7.3 Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the fritted support.

7.4 Shake the sample vigorously and quantitatively transfer the predetermined sample volume selected in 7.2 to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.

7.5 With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.

NOTE: Total volume of wash water used should equal approximately 2 ml per cm^2. For a 4.7 cm filter the total volume is 30 ml.

7.6 Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103–105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).

8. Calculations

8.1 Calculate non-filterable residue as follows:

$$\text{Non-filterable residue, mg/l} = \frac{(A - B)\times 1{,}000}{C}$$

where:

A = weight of filter (or filter and crucible) + residue in mg
B = weight of filter (or filter and crucible) in mg
C = ml of sample filtered

9. Precision and Accuracy

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual samples cannot be obtained.

Bibliography

1. NCASI Technical Bulletin No. 291, March 1977. National Council of the Paper Industry for Air and Stream Improvement, Inc., 260 Madison Ave., NY.

RESIDUE, TOTAL

Method 160.3 (Gravimetric, Dried at 103–105°C)

STORET NO. 00500

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The practical range of the determination is from 10 mg/1 to 20,000 mg/1.
2. Summary of Method
   2.1 A well mixed aliquot of the sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103–105°C.
3. Definitions
   3.1 Total Residue is defined as the sum of the homogenous suspended and dissolved materials in a sample.
4. Sample Handling and Preservation
   4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   5.1 Non-representative particulates such as leaves, sticks, fish and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
   5.2 Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.
6. Apparatus
   6.1 Evaporating dishes, porcelain, 90 mm, 100 ml capacity. (Vycor or platinum dishes may be substituted and smaller size dishes may be used if required.)
7. Procedure
   7.1 Heat the clean evaporating dish to 103–105°C for one hour, if Volatile Residue is to be measured, heat at 550 ±50°C for one hour in a muffle furnace. Cool, desiccate, weigh and store in desiccator until ready for use.
   7.2 Transfer a measured aliquot of sample to the pre-weighed dish and evaporate to dryness on a steam bath or in a drying oven.
      7.2.1 Choose an aliquot of sample sufficient to contain a residue of at least 25 mg. To obtain a weighable residue, successive aliquots of sample may be added to the same dish.
      7.2.2 If evaporation is performed in a drying oven, the temperature should be lowered to approximately 98°C to prevent boiling and splattering of the sample.

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7.3 Dry the evaporated sample for at least 1 hour at 103–105°C. Cool in a desiccator and weigh. Repeat the cycle of drying at 103–105°C, cooling, desiccating and weighing until a constant weight is obtained or until loss of weight is less than 4% of the previous weight, or 0.5 mg, whichever is less.

8. Calculation

8.1 Calculate total residue as follows:

$$\text{Total residue, mg/l} = \frac{(A - B)\times 1{,}000}{C}$$

where:

A = weight of sample + dish in mg
B = weight of dish in mg
C = volume of sample in ml

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 91, Method 208A, (1975).

RESIDUE, VOLATILE

Method 160.4 (Gravimetric, Ignition at 550°C)

STORET NO. Total 00505
Non-Filterable 00535
Filterable 00520

1. Scope and Application
   - 1.1 This method determines the weight of solid material combustible at 550°C.
   - 1.2 The test is useful in obtaining a rough approximation of the amount of organic matter present in the solid fraction of sewage, activated sludge, industrial wastes, or bottom sediments.
2. Summary of Method
   - 2.1 The residue obtained from the determination of total, filterable or non-filterable residue is ignited at 550°C in a muffle furnace. The loss of weight on ignition is reported as mg/1 volatile residue.
3. Comments
   - 3.1 The test is subject to many errors due to loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.
   - 3.2 The results should not be considered an accurate measure of organic carbon in the sample, but may be useful in the control of plant operations.
   - 3.3 The principal source of error in the determination is failure to obtain a representative sample.
4. Sample Handling and Preservation
   - 4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decompostion of solids is recommended.
5. Precision and Accuracy
   - 5.1 A collaborative study involving three laboratories examining four samples by means of ten replicates showed a standard deviation of ±11 mg/1 at 170 mg/1 volatile residue concentration.
6. Reference
   - 6.1 The procedure to be used for this determination is found in:
     Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 95, Method 208E, (1975).

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SETTLEABLE MATTER

Method 160.5 (Volumetric, Imhoff Cone)

STORET NO. 50086

1. Scope and Application
   - 1.1 This method is applicable to surface and saline waters, domestic and industrial wastes.
   - 1.2 The practical lower limit of the determination is about 0.2 ml/l/hr.
2. Summary of Method
   - 2.1 Settleable matter is measured volumetrically with an Imhoff cone.
3. Comments
   - 3.1 For some samples, a separation of settleable and floating materials will occur; in such cases the floating materials are not measured.
   - 3.2 Many treatment plants, especially plants equipped to perform gravimetric measurements, determine residue non-filterable (suspended solids), in preference to settleable matter, to insure that floating matter is included in the analysis.
4. Precision and Accuracy
   - 4.1 Data on this determination are not available at this time.
5. References
   - 5.1 The procedure to be used for this determination is found in:
     Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 95, Method 208F, Procedure 3a (1975).

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TEMPERATURE

Method 170.1 (Thermometric)

STORET NO. 00010

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
   2.1 Temperature measurements may be made with any good grade of mercury-filled or dial type centigrade thermometer, or a thermistor.
3. Comments
   3.1 Measurement device should be routinely checked against a precision thermometer certified by the National Bureau of Standards.
4. Precision and Accuracy
   4.1 Precision and accuracy for this method have not been determined.
5. Reference
   5.1 The procedure to be used for this determination is found in:
   Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 125, Method 212 (1975).

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TURBIDITY
Method 180.1 (Nephelometric)

STORET NO. 00076

1. Scope and Application
    1.1 This method is applicable to drinking, surface, and saline waters in the range of turbidity from 0 to 40 nephelometric turbidity units (NTU). Higher values may be obtained with dilution of the sample.

    NOTE 1: NTU's are considered comparable to the previously reported Formazin Turbidity Units (FTU) and Jackson Turbidity Units (JTU).
2. Summary of Method
    2.1 The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Readings, in NTU's, are made in a nephelometer designed according to specifications outlined in Apparatus. A standard suspension of Formazin, prepared under closely defined conditions, is used to calibrate the instrument.
        2.1.1 Formazin polymer is used as the turbidity reference suspension for water because it is more reproducible than other types of standards previously used for turbidity standards.
        2.1.2 A commercially available polymer standard is also approved for use for the National Interim Primary Drinking Water Regulations. This standard is identified as AMCO-AEPA-1 available from Amco Standard International, Inc.
3. Sample Handling and Preservation
    3.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
4. Interferences
    4.1 The presence of floating debris and coarse sediments which settle out rapidly will give low readings. Finely divided air bubbles will affect the results in a positive manner.
    4.2 The presence of true color, that is the color of water which is due to dissolved substances which absorb light, will cause turbidities to be low, although this effect is generally not significant with finished waters.
5. Apparatus
    5.1 The turbidimeter shall consist of a nephelometer with light source for illuminating the sample and one or more photo-electric detectors with a readout device to indicate the intensity of light scattered at right angles to the path of the incident light. The turbidimeter should be so designed that little stray light reaches the detector in the

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absence of turbidity and should be free from significant drift after a short warm-up period.

5.2 The sensitivity of the instrument should permit detection of a turbidity difference of 0.02 unit or less in waters having turbidities less than 1 unit. The instrument should measure from 0 to 40 units turbidity. Several ranges will be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities.

5.3 The sample tubes to be used with the available instrument must be of clear, colorless glass. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched. They must not be handled at all where the light strikes them, but should be provided with sufficient extra length, or with a protective case, so that they may be handled.

5.4 Differences in physical design of turbidimeters will cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, the following design criteria should be observed:

5.4.1 Light source: Tungsten lamp operated at a color temperature between 2200–3000°K.

5.4.2 Distance traversed by incident light and scattered light within the sample tube: Total not to exceed 10 cm.

5.4.3 Detector: Centered at 90° to the incident light path and not to exceed ±30° from 90°. The Detector, and filter system if used, shall have a spectral peak response between 400 and 600nm.

5.5 The Hach Turbidimeter, Model 2100 and 2100 A, is in wide use and has been found to be reliable; however, other instruments meeting the above design criteria are acceptable.

6. Reagents

6.1 Turbidity-free water: Pass distilled water through a 0.45*u* pore size membrane filter if such filtered water shows a lower turbidity than the distilled water.

6.2 Stock formazin turbidity suspension:

Solution 1: Dissolve 1.00 g hydrazine sulfate, $(NH_2)_2 \bullet H_2SO_4$, in distilled water and dilute to 100 ml in a volumetric flask.

Solution 2: Dissolve 10.00 g hexamethylenetetramine in distilled water and dilute to 100 ml in a volumetric flask.

In a 100 ml volumetric flask, mix 5.0 ml Solution 1 with 5.0 ml Solution 2. Allow to stand 24 hours at 25 ±3°C, then dilute to the mark and mix.

6.3 Standard formazin turbidity suspension: Dilute 10.00 ml stock turbidity suspension to 100 ml with turbidity-free water. The turbidity of this suspension is defined as 40 units. Dilute portions of the standard turbidity suspension with turbidity-free water as required.

6.3.1 A new stock turbidity suspension should be prepared each month. The standard turbidity suspension and dilute turbidity standards should be prepared weekly by dilution of the stock turbidity suspension.

6.4 The AMCO-AEPA-1 standard as supplied requires no preparation or dilution prior to use.

7. Procedure

7.1 Turbidimeter calibration: The manufacturer's operating instructions should be followed. Measure standards on the turbidimeter covering the range of interest. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration scales. At least one standard should be run in each instrument range to be used. Some instruments permit adjustments of sensitivity so that scale values will correspond to turbidities. Reliance on a manufacturer's solid scattering standard for setting overall instrument sensitivity for all ranges is not an acceptable practice unless the turbidimeter has been shown to be free of drift on all ranges. If a pre-calibrated scale is not supplied, then calibration curves should be prepared for each range of the instrument.

7.2 Turbidities less than 40 units: Shake the sample to thoroughly disperse the solids. Wait until air bubbles disappear then pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

7.3 Turbidities exceeding 40 units: Dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor. For example, if 5 volumes of turbidity-free water were added to 1 volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample was 180 units.

7.3.1 The Hach Turbidimeters, Models 2100 and 2100A, are equipped with 5 separate scales: 0–0.2, 0–1.0, 0–100, and 0–1000 NTU. The upper scales are to be used only as indicators of required dilution volumes to reduce readings to less than 40 NTU. **NOTE 2:** Comparative work performed in the MDQAR Laboratory indicates a progressive error on sample turbidities in excess of 40 units.

8. Calculation

8.1 Multiply sample readings by appropriate dilution to obtain final reading.

8.2 Report results as follows:

NTU	Record to Nearest:
0.0 – 1.0	0.05
1 – 10	0.1
10 – 40	1
40 – 100	5
100 – 400	10
400 – 1000	50
> 1000	100

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using surface water samples at levels of 26, 41, 75 and 180 NTU, the standard deviations were ±0.60, ±0.94, ±1.2 and ±4.7 units, respectively.

9.2 Accuracy data are not available at this time.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D1889–71, p 223 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 132, Method 214A, (1975).

METALS

(Atomic Absorption Methods)

1. Scope and Application
   1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. While drinking waters free of particulate matter may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper pretreatment.
   1.2 Detection limits, sensitivity and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The data shown in Table 1, however, provide some indication of the actual concentration ranges measurable by direct aspiration and using furnace techniques. In the majority of instances the concentration range shown in the table by direct aspiration may be extended much lower with scale expansion and conversely extended upwards by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. Lower concentrations may also be determined using the furnace techniques. The concentration ranges given in Table 1 are somewhat dependent on equipment such as the type of spectrophotometer and furnace accessory, the energy source and the degree of electrical expansion of the output signal. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To insure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see 5.2.1) and if detected, treat accordingly using either successive dilution, matrix modification or method of standard additions (see 8.5).
   1.3 Where direct aspiration atomic absorption techniques do not provide adequate sensitivity, in addition to the furnace procedure, reference is made to specialized procedures such as the gaseous hydride method for arsenic and selenium, the cold vapor technique for mercury, and the chelation–extraction procedure for selected metals. Reference to approved colorimetric methods is also made.
   1.4 Atomic absorption procedures are provided as the methods of choice; however, other instrumental methods have also been shown to be capable of producing precise and accurate analytical data. These instrumental techniques include emission spectroscopy, X-ray fluorescence, spark source mass spectroscopy, and anodic stripping to name but a few. The analyst should be cautioned that these methods are highly specialized techniques requiring a high degree of skill to interpret results and obtain valid data.

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These above mentioned techniques are presently considered as alternate test procedures and approval must be obtained prior to their use.

2. Summary of Method

2.1 In direct aspiration atomic absorption spectroscopy a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp whose cathode is made of the element to be determined is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.2 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy (Spectrochim Acta, *24B* 53, 1969) the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2.1 Preliminary treatment of wastewater and/or industrial effluents is usually necessary because of the complexity and variability of the sample matrix. Suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. When the breakdown of organic material is necessitated, the process should include a wet digestion with nitric acid.

2.2.2 In those instances where complete characterization of a sample is desired, the suspended material must be analyzed separately. This may be accomplished by filtration and acid digestion of the suspended material. Metallic constituents in this acid digest are subsequently determined and the sum of the dissolved plus suspended concentrations will then provide the total concentrations present. The sample should be filtered as soon as possible after collection and the filtrate acidified immediately.

2.2.3 The total sample may also be treated with acid without prior filtration to measure what may be termed "total recoverable" concentrations.

2.3 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms are vaporized and dissociated for absorption in the tube than the flame, the use of small sample volumes or detection of low concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor.

TABLE 1

Atomic Absorption Concentration Ranges(1)

	Direct Aspiration			Furnace Procedure(4,5)	
Metal	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l	Detection Limit ug/l	Optimum Concentration Range ug/l
Aluminum	0.1	1	5 – 50	3	20 – 200
Antimony	0.2	0.5	1 – 40	3	20 – 300
Arsenic(2)	0.002	–	0.002 – 0.02	1	5 – 100
Barium(p)	0.1	0.4	1 – 20	2	10 – 200
Beryllium	0.005	0.025	0.05 – 2	0.2	1 – 30
Cadmium	0.005	0.025	0.05 – 2	0.1	0.5 – 10
Calcium	0.01	0.08	0.2 – 7	–	– –
Chromium	0.05	0.25	0.5 – 10	1	5 – 100
Cobalt	0.05	0.2	0.5 – 5	1	5 – 100
Copper	0.02	0.1	0.2 – 5	1	5 – 100
Gold	0.1	0.25	0.5 – 20	1	5 – 100
Iridium(p)	3	8	20 – 500	30	100 – 1500
Iron	0.03	0.12	0.3 – 5	1	5 – 100
Lead	0.1	0.5	1 – 20	1	5 – 100
Magnesium	0.001	0.007	0.02 – 0.5	–	– –
Manganese	0.01	0.05	0.1 – 3	0.2	1 – 30
Mercury(3)	0.0002	–	0.0002 – 0.01	–	– –
Molybdenum(p)	0.1	0.4	1 – 40	1	3 – 60
Nickel(p)	0.04	0.15	0.3 – 5	1	5 – 50
Osmium	0.3	1	2 – 100	20	50 – 500
Palladium(p)	0.1	0.25	0.5 – 15	5	20 – 400
Platinum(p)	0.2	2	5 – 75	20	100 – 2000
Potassium	0.01	0.04	0.1 – 2	–	–
Rhenium(p)	5	15	50 – 1000	200	500 – 5000
Rhodium(p)	0.05	0.3	1 – 30	5	20 – 400
Ruthenium	0.2	0.5	1 – 50	20	100 – 2000
Selenium(2)	0.002	–	0.002 – 0.02	2	5 – 100
Silver	0.01	0.06	0.1 – 4	0.2	1 – 25
Sodium	0.002	0.015	0.03 – 1	–	– –
Thallium	0.1	0.5	1 – 20	1	5 – 100
Tin	0.8	4	10 – 300	5	20 – 300
Titanium (p)	0.4	2	5 – 100	10	50 – 500
Vanadium (p)	0.2	0.8	2 – 100	4	10 – 200
Zinc	0.005	0.02	0.05 – 1	0.05	0.2 – 4

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(1) The concentrations shown are not contrived values and should be obtainable with any satisfactory atomic absorption spectrophotometer.

(2) Gaseous hydride method.

(3) Cold vapor technique.

(4) For furnace sensitivity values consult instrument operating manual.

(5) The listed furnace values are those expected when using a 20 ul injection and normal gas flow except in the case of arsenic and selenium where gas interrupt is used. The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

3. Definition of Terms

3.1 Optimum Concentration Range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating condition employed.

3.2 Sensitivity: The concentration in milligrams of metal per liter that produces an absorption of 1%.

3.3 Detection Limit: Detection limits can be expressed as either an instrumental or method parameter. The limiting factor of the former using acid water standards would be the signal to noise ratio and degree of scale expansion used; while the latter would be more affected by the sample matrix and preparation procedure used. The Scientific Apparatus Makers Association (SAMA) has approved the following definition for detection limit: that concentration of an element which would yield an absorbance equal to twice the standard deviation of a series of measurements of a solution, the concentraton of which is distinctly detectable above, but close to blank absorbance measurement. The detection limit values listed in Table I and on the individual analysis sheets are to be considered minimum working limits achievable with the procedures given in this manual. These values may differ from the optimum detection limit reported by the various instrument manufacturers.

3.4 Dissolved Metals: Those constituents (metals) which will pass through a 0.45 u membrane filter.

3.5 Suspended Metals: Those constituents (metals) which are retained by a 0.45 u membrane filter.

3.6 Total Metals: The concentration of metals determined on an unfiltered sample following vigorous digestion (Section 4.1.3), or the sum of the concentrations of metals in both the dissolved and suspended fractions.

3.7 Total Recoverable Metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Section 4.1.4).

4. Sample Handling and Preservation

4.1 For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. The sample bottle whether borosilicate glass, polyethylene polypropylene or Teflon should be thoroughly washed with detergent and tap water; rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and finally deionized distilled water in that order.

NOTE 1: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product—NOCHROMIX—available from Godax Laboratories, 6 Varick St. New York, N.Y. 10013, may be used in place of chromic acid. [Chromic acid should not be used with plastic bottles.]

NOTE 2: If it can be documented through an active analytical quality control program using spiked samples, reagent and sample blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

Before collection of the sample a decision must be made as to the type of data desired, i.e., dissolved, suspended, total or total recoverable. For container preference, maximum holding time and sample preservation at time of collection see Table 1 in the front part of this manual. Drinking water samples containing suspended and setteable material should be prepared using the total recoverable metal procedure (section 4.1.4).

4.1.1 For the determination of dissolved constituents the sample must be filtered through a 0.45 u membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus using plain, non-grid marked, membrane filters are recommended to avoid possible contamination.) Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of <2. Normally, 3 ml of (1:1) acid per liter should be sufficient to preserve the sample (See Note 3). If hexavalent chromium is to be included in the analytical scheme, a portion of the filtrate should be transferred before acidification to a separate container and analyzed as soon as possible using Method 218.4. Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

NOTE 3: If a precipitate is formed upon acidification, the filtrate should be digested using 4.1.3. Also, it has been suggested (International Biological Program, Symposium on Analytical Methods, Amsterdam, Oct. 1966) that additional acid, as much as 25 ml of conc. HCl/liter, may be required to stabilize certain types of highly buffered samples if they are to be stored for any length of time. Therefore, special precautions should be observed for preservation and storage of unusual samples intended for metal analysis.

4.1.2 For the determination of suspended metals a representative volume of unpreserved sample must be filtered through a 0.45 *u* membrane filter. When considerable suspended material is present, as little as 100 ml of a well mixed sample is filtered. Record the volume filtered and transfer the membrane filter containing the insoluble material to a 250 ml Griffin beaker and add 3 ml conc. redistilled HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 ml of conc. redistilled HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (DO NOT BAKE), add 5 ml distilled HCl (1:1) and warm the beaker gently to dissolve any soluble material. (If the sample is to be analyzed by the furnace procedure, 1 ml of 1:1 distilled HNO_3 per 100 ml dilution should be substituted for the distilled 1:1 HCl.) Wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected concentrations of metals present. This volume will vary depending on the metal to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended" (See Note 4.)

NOTE 4: Certain metals such as antimony arsenic, gold, iridium, mercury, osmium, palladium, platinium, rhenium, rhodium, ruthenium, selenium, silver, thallium, tin and titanium require modification of the digestion procedure and the individual sheets for these metals should be consulted.

4.1.3 For the determination of total metals the sample is acidified with 1:1 redistilled HNO_3 to a pH of less than 2 at the time of collection. The sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50–100 ml of well mixed sample will most probably be sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined.)

Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. redistilled HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3 ml portion of conc. redistilled HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of redistilled 1:1 HCl (5 ml/100 ml of final solution) and warm the beaker to dissolve any precipitate or residue resulting from evaporation. (If the sample is to be analyzed by the furnace procedure, substitute distilled HNO_3 for 1:1 HCl so that the final dilution contains 0.5% (v/v) HNO_3.) Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total" (see Note 4).

4.1.4 To determine total recoverable metals, acidify the entire sample at the time of collection with conc. redistilled HNO_3, 5 ml/1. At the time of analysis a 100 ml aliquot of well mixed sample is transferred to a beaker or flask. Five ml of distilled HCl (1:1) is added and the sample heated on a steam bath or hot plate until the volume has been reduced to 15–20 ml making certain the samples do not boil. (If the sample is being prepared for furnace analysis, the same process should be followed except HCl should be omitted.) After this treatment the sample is filtered to remove silicates and other insoluble material that could clog the atomizer and the volume adjusted to 100 ml. The sample is then ready for analysis. Concentrations so determined shall be reported as "total". (See Notes 4, 5, and 6.)

NOTE 5: The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy certain metal complexes if a colorimetric procedure is to be employed for the final determination. When this is suspect, the more vigorous digestion given in 4.1.3 should be followed.

NOTE 6: For drinking water analyses by direct aspiration, the final volume may be reduced to effect up to a 10X concentration of the sample, provided the total dissolved solids in the original sample do not exceed 500 mg/1, the determination is corrected for any non-specific absorbance and there is no loss by precipitation.

5. Interferences

5.1 Direct Aspiration

5.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium, calcium and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

5.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are primarily employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

5.1.3 The presence of high dissolved solids in the sample may result in an interference from non-atomic absorbance such as light scattering. If background correction is not available, a non-absorbing wavelength should be checked. Preferably, high solids type samples should be extracted (see 5.1.1 and 9.2).

5.1.4 Ionization interferences occur where the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positive charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess of an easily ionized element.

5.1.5 Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-element lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

5.2 Flameless Atomization

5.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference use the following procedure. Withdraw from the sample two equal aliquots. To one of the aliquots add a known amount of analyte and dilute both aliquots to the same predetermined volume. [The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4 while keeping in mind the optimum concentration range of the analysis. Under no circumstances should the dilution be less than 1:1]. The diluted aliquots should then be analyzed and the unspiked results multiplied by the dilution factor should be compared to the original determination. Agreement of the results (within ±10%) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis. Those samples which indicate the presence of interference, should be treated in one or more of the following ways.

a. The samples should be successively diluted and reanalyzed to determine if the interference can be eliminated.

b. The matrix of the sample should be modified in the furnace. Examples are the addition of ammonium nitrate to remove alkali chlorides, ammonium phosphate to retain cadmium, and nickel nitrate for arsenic and selenium analyses [ATOMIC ABSORPTION NEWSLETTER Vol. 14, No. 5, p 127, Sept-Oct 1975]. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

c. Analyze the sample by method of standard additions while noting the precautions and limitations of its use (See 8.5).

5.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either the use of background correction or choosing an alternate wavelength outside the absorption band should eliminate this interference. Non-specific broad band absorption interference can also be compensated for with background correction.

5.2.3 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analysis element.

5.2.4 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way broad band absorption will be minimized.

5.2.5 From anion interference studies in the graphite furnace it is generally accepted that nitrate is the preferred anion. Therefore nitric acid is preferable for any digestion or solubilization step. If another acid in addition to $HN0_3$ is required a minimum amount should be used. This applies particularly to hydrochloric and to a lesser extent to sulfuric and phosphoric acids.

5.2.6 Carbide formation resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. Molybdenum may be cited as an example. When this takes place, the metal will be released very slowly from the carbide as atomization continues. For molybdenum, one may be required to atomize for 30 seconds or more before the signal returns to baseline levels. This problem is greatly reduced and the sensitivity increased with the use of pyrolytically-coated graphite.

5.2.7 Ionization interferences have to date not been reported with furnace techniques.

5.2.8 For comments on spectral interference see section 5.1.5.

5.2.9 Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in part 6.9 of the Atomic Absorption Methods section of this manual. Pipet tips have been known to be a source of contamination. If suspected, they should be acid soaked with 1:5 HNO_3 and rinsed thoroughly with tap and deionized water. The use of a better grade pipet tip can greatly reduce this problem. It is very important that special attention be given to reagent blanks in both analysis and the correction of analytical results. Lastly, pyrolytic graphite because of the production process and handling can become contaminated. As many as five to possibly ten high temperature burns may be required to clean the tube before use.

6. Apparatus

6.1 Atomic absorption spectrophotometer: Single or dual channel, single-or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip chart recorder.

6.2 Burner: The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

6.3 Hollow cathode lamps: Single element lamps are to be preferred but multi-element lamps may be used. Electrodeless discharge lamps may also be used when available.

6.4 Graphite furnace: Any furnace device capable of reaching the specified temperatures is satisfactory.

6.5 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can be easily recognized.

6.6 Pipets: Microliter with disposable tips. Sizes can range from 5 to 100 microliters as required. **NOTE 7**: Pipet tips which are white in color, do not contain CdS, and have been found suitable for research work are available from Ulster Scientific, Inc. 53 Main St. Highland, NY 12528 (914) 691–7500.

6.7 Pressure-reducing valves: The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

6.8 Separatory flasks: 250 ml, or larger, for extraction with organic solvents.

6.9 Glassware: All glassware, linear polyethylene, polyproplyene or Teflon containers, including sample bottles, should be washed with detergent, rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and deionized distilled water in that order. [See Notes 1 and 2 under (4.1) concerning the use of chromic acid and the cleaning procedure.]

6.10 Borosilicate glass distillation apparatus.

7. Reagents

7.1 Deionized distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

7.2 Nitric acid (conc.): If metal impurities are found to be present, distill reagent grade nitric acid in a borosilicate glass distillation apparatus or use a spectrograde acid.
Caution: Distillation should be performed in hood with protective sash in place.

7.2.1 Nitric Acid (1:1): Prepare a 1:1 dilution with deionized, distilled water by adding the conc. acid to an equal volume of water.

7.3 Hydrochloric acid (1:1): Prepare a 1:1 solution of reagent grade hydrochloric acid and deionized distilled water. If metal impurities are found to be present, distill this mixture from a borosilicate glass distillation apparatus or use a spectrograde acid.

7.4 Stock standard metal solutions: Prepare as directed in (8.1) and under the individual metal procedures. Commercially available stock standard solutions may also be used.

7.5 Calibration standards: Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

7.6 Fuel and oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

7.7 Special reagents for the extraction procedure.

7.7.1 Pyrrolidine dithiocarbamic acid (PDCA) "see footnote": Prepare by adding 18 ml of analytical reagent grade pyrrolidine to 500 ml of chloroform in a liter flask.

The name pyrrolidine dithiocarbamic acid (PDCA), although commonly referenced in the scientific literature is ambiguous. From the chemical reaction of pyrrolidine and carbon disulfide a more proper name would be 1-pyrrolidine carbodithioic acid, PCDA (CAS Registry No. 25769–03–3).

(See **Note 8**) Cool and add 15 ml of carbon disulfide in small portions and with swirling. Dilute to 1 liter with chloroform. The solution can be used for several months if stored in a brown bottle in a refrigerator.

NOTE 8: An acceptable grade of pyrrolidine may be obtained from the Aldrich Chemical Co., 940 West St. Paul Ave., Milwaukee, WI. 53233 (414, 273–3850).

7.7.2 Ammonium hydroxide, 2N: Dilute 13 ml conc. NH_4OH to 100 ml with deionized distilled water.

7.7.3 Bromophenol blue indicator (1 g/liter): Dissolve 0.1 g bromophenol blue in 100 ml of 50 percent ethanol or isopropanol.

7.7.4 HCl, 2.5% v/v: Dilute 2 ml redistilled HCl (6N) to 40 ml with deionized distilled water.

8. Preparation of Standards and Calibration

8.1 Stock standard solutions are prepared from high purity metals, oxides or nonhygroscopic reagent grade salts using deionized distilled water and redistilled nitric or hydrochloric acids. (See individual analysis sheets for specific instruction.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1000 mg of the metal per liter. Commercially available standard solutions may also be used.

8.2 Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least four calibration standards in graduated amounts in the appropriate range. The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. As filtered water samples are preserved with 1:1 redistilled HNO_3 (3 ml per liter), calibration standards for these analyses should be similarly prepared with HNO_3. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal.

8.3 Where the sample matrix is so complex that viscosity, surface tension and components cannot be accurately matched with standards, the method of standard addition must be used. This technique relies on the addition of small, known amounts of the analysis element to portions of the sample—the absorbance difference between those and the original solution giving the slope of the calibration curve. The method of standard addition is described in greater detail in (8.5).

8.4 For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorption of 0 to 80 percent. The correct method is to convert the percent absorption readings to absorbance and plot that value against concentration. The following relationship is used to convert absorption values to absorbance:

absorbance = log (100/%T) = 2–log % T
where % T = 100–% absorption

As the curves are frequently nonlinear, especially at high absorption values, the number of standards should be increased in that portion of the curve.

8.5 Method of Standard Additions: In this method, equal volumes of sample are added to a deionized distilled water blank and to three standards containing different known amounts of the test element. The volume of the blank and the standards must be the same. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Fig. 1.

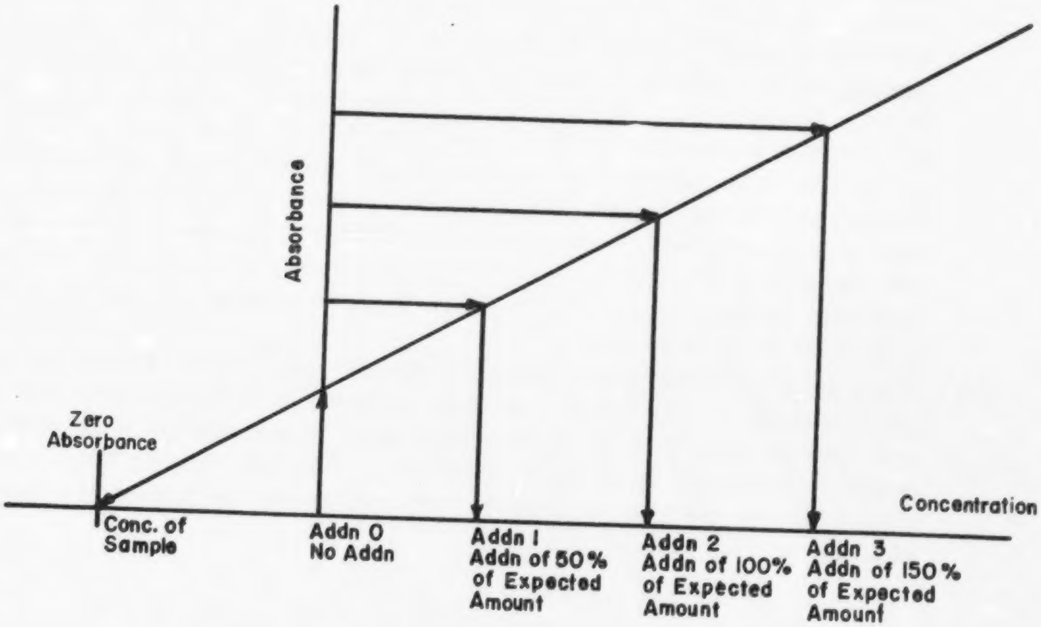

FIGURE 1. STANDARD ADDITION PLOT

The method of standard additions can be very useful, however, for the results to be valid the following limitations must be taken into consideration:

a) the absorbance plot of sample and standards must be linear over the concentration range of concern. For best results the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20%) caution should be exercised.

b) the effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes and the standard addition should respond in a similar manner as the analyte.

c) the determination must be free of spectral interference and corrected for non-specific background interference.

9. General Procedure for Analysis by Atomic Absorption

9.1 Direct Aspiration: Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for his particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes unless operated in a double beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the manufactuerer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis and construct a calibration curve by plotting the concentrations of the standards against the absorbance. For those instruments which read directly in concentration set the curve corrector to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples are run.

9.1.1 Calculation - Direct determination of liquid samples: Read the metal value in mg/1 from the calibration curve or directly from the readout system of the instrument.

9.1.1.1 If dilution of sample was required:

$$\text{mg/l metal in sample} = A \left(\frac{C + B}{C}\right)$$

where:

A = mg/1 of metal indiluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

9.1.2 For samples containing particulates:

$$\text{mg/l metal in sample} = A\left(\frac{V}{C}\right)$$

where:

A = mg/1 of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
C = ml of sample aliquot processed

9.1.3 For solid samples: report all concentrations as mg/kg dry weight

9.1.3.1 Dry sample:

$$\text{mg metal/kg sample} = \frac{A \times V}{D}$$

where:

A = mg/1 of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
D = weight of dry sample in grams

9.1.3.2 Wet sample:

$$\text{mg metal/kg sample} = \frac{A \times V}{W \times P}$$

where:

A = mg/1 of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
W = weight of wet sample in grams
P = % solids

9.2 Special Extraction Procedure: When the concentration of the metal is not sufficiently high to determine directly, or when considerable dissolved solids are present in the sample, certain metals may be chelated and extracted with organic solvents. Ammonium pyrrolidine dithiocarbamate (APDC) (see footnote) in methyl isobutyl ketone (MIBK) is widely used for this purpose and is particularly useful for zinc, cadmium, iron, manganese, copper, silver, lead and chromium^{+6}. Tri-valent chromium does not react with APDC unless it has first been converted to the hexavalent form [Atomic Absorption Newsletter *6*, p 128 (1967)]. This procedure is described under method 218.3.

The name ammonium pyrrolidine dithiocarbamate (APDC) is somewhat ambiguous and should more properly be called ammonium, 1-pyrrolidine carbodithioate (APCD), CAS Registry No. 5108-96-3.

Aluminum, beryllium, barium and strontium also do not react with APDC. While the **APDC-MIBK** chelating-solvent system can be used satisfactorily, it is possible to experience difficulties. (See Note 9.)

NOTE 9: Certain metal chelates, manganese-APDC in particular, are not stable in MIBK and will redissolve into the aqueous phase on standing. The extraction of other metals is sensitive to both shaking rate and time. As with cadmium, prolonged extraction beyond 1 minute, will reduce the extraction efficiency, whereas 3 minutes of vigorous shaking is required for chromium.

Also, when multiple metals are to be determined either larger sample volumes must be extracted or individual extractions made for each metal being determined. The acid form of APDC-pyrrolidine dithiocarbamic acid prepared directly in chloroform as described by Lakanen, [Atomic Absorption Newsletter *5*, p 17 (1966)], (see 7.7.1) has been found to be most advantageous. In this procedure the more dense chloroform layer allows for easy combination of multiple extractions which are carried out over a broader pH range favorable to multielement extractions. Pyrrolidine dithiocarbamic acid in chloroform is very stable and may be stored in a brown bottle in the refrigerator for months. Because chloroform is used as the solvent, it may not be aspirated into the flame. The following procedure is suggested.

9.2.1 Extraction procedure with pyrrolidine dithiocarbamic acid (PDCA) in chloroform.

9.2.1.1 Transfer 200 ml of sample into a 250 ml separatory funnel, add 2 drops bromphenol blue indicator solution (7.7.3) and mix.

9.2.1.2 Prepare a blank and sufficient standards in the same manner and adjust the volume of each to approximately 200 ml with deionized distilled water. All of the metals to be determined may be combined into single solutions at the appropriate concentration levels.

9.2.1.3 Adjust the pH by addition of 2N NH_4OH solution (7.7.2) until a blue color persists. Add HCl (7.7.4) dropwise until the blue color just disappears; then add 2.0 ml HCl (7.7.4) in excess. The pH at this point should be 2.3. (The pH adjustment may be made with a pH meter instead of using indicator.)

9.2.1.4 Add 5 ml of PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and drain the chloroform layer into a 100 ml beaker. (See NOTE 10.)

NOTE 10: If hexavalent chromium is to be extracted, the aqueous phase must be readjusted back to a pH of 2.3 after the addition of PDCA–chloroform and maintained at that pH throughout the extraction. For multielement extraction, the pH may adjusted upward after the chromium has been extracted.

9.2.1.5 Add a second portion of 5 ml PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and combine the chloroform phase with that obtained in step (9.2.1.4).

9.2.1.6 Determine the pH of the aqueous phase and adjust to 4.5.

9.2.1.7 Repeat step (9.2.1.4) again combining the solvent extracts.

9.2.1.8 Readjust the pH to 5.5, and extract a fourth time. Combine all extracts and evaporate to dryness on a steam bath.

9.2.1.9 Hold the beaker at a 45 degree angle, and slowly add 2 ml of conc. distilled nitric acid, rotating the beaker to effect thorough contact of the acid with the residue.

9.2.1.10 Place the beaker on a low temperature hotplate or steam bath and evaporate just to dryness.

9.2.1.11 Add 2 ml of nitric acid (1:1) to the beaker and heat for 1 minute. Cool, quantitatively transfer the solution to a 10 ml volumetric flask and bring to volume with distilled water. The sample is now ready for analysis.

9.2.2 Prepare a calibration curve by plotting absorbance versus the concentration of the metal standard (*u*g/l) in the 200 ml extracted standard solution. To calculate sample concentration read the metal value in *u*g/l from the calibration curve or directly from the readout system of the instrument. If dilution of the sample was required use the following equation:

$$\text{mg/l metal in sample} = Z\left(\frac{C + B}{C}\right)$$

where:

Z = *u*g/l of metal in diluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

9.3 Furnace Procedure: Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instuctions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of his particular instrument and use as a guide the temperature settings and other instrument conditions listed on the individual analysis sheets which are recommended for the Perkin-Elmer HGA-2100. In addition, the following points may be helpful.

9.3.1 With flameless atomization, background correction becomes of high importance especially below 350 nm. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. It can be caused by the presence of gaseous molecular species, salt particules, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

9.3.2 If during atomization all the analyte is not volatilized and removed from the furnace, memory effects will occur. This condition is dependent on several factors such as the volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization and furnace design. If this situation is detected through blank burns, the tube should be cleaned by operating the furnace at full power for the required time period as needed at regular intervals in the analytical scheme.

9.3.3 Some of the smaller size furnace devices, or newer furnaces equipped with feedback temperature control (Instrumentation Laboratories MODEL 555, Perkin-Elmer MODELS HGA 2200 and HGA 76B, and Varian MODEL CRA-90) employing faster rates of atomization, can be operated using lower atomization temperatures for shorter time periods than those listed in this manual.

9.3.4 Although prior digestion of the sample in many cases is not required providing a representative aliquot of sample can be pipeted into the furnace, it will provide for a more uniform matrix and possibly lessen matrix effects.

9.3.5 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

9.3.6 To verify the absence of interference, follow the procedure as given in part 5.2.1.

9.3.7 A check standard should be run approximately after every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Even though tube life depends on sample matrix and atomization temperature, a conservative estimate would be that a tube will last at least 50 firings. A pyrolytic-coating would extend that estimate by a factor of 3.

9.3.8 Calculation–For determination of metal concentration by the furnace: Read the metal value in *u*g/1 from the calibration curve or directly from the readout system of the instrument.

9.3.8.1 If different size furnace injection volumes are used for samples than for standards:

$$ug/l \text{ of metal in sample} = Z \left(\frac{S}{U}\right)$$

where:

Z = *u*g/1 of metal read from calibration curve or readout system
S = ul volume standard injected into furnace for calibration curve
U = ul volume of sample injected for analysis

9.3.8.2 If dilution of sample was required but sample injection volume same as for standard:

$$\mu g/l \text{ of metal in sample} = Z \left(\frac{C + B}{C}\right)$$

where:

Z = ug/1 metal in diluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

9.3.9 For sample containing particulates:

$$\mu g/l \text{ of metal in sample} = Z \left(\frac{V}{C}\right)$$

where:

Z = ug/1 of metal in processed sample from calibration curve (See 9.3.8.1)
V = final volume of processed sample in ml
C = ml of sample aliquot processed

9.3.10 For solid samples: Report all concentrations as mg/kg dry weight

9.3.10.1 Dry sample:

$$\text{mg metal/kg sample} = \frac{\left(\frac{Z}{1,000}\right) V}{D}$$

where:

Z = ug/1 of metal in processed sample from calibration curve (See 9.3.8.1)
V = final volume of processed sample in ml
D = weight of dry sample in grams

9.3.10.2 Wet sample:

$$\text{mg metal/kg sample} = \frac{\left(\frac{Z}{1,000}\right) V}{W \times P}$$

where:

Z = ug/1 of metal in processed sample from calibration curve (See 9 3.8.1)
V = final volume of processed sample in ml
W = weight of wet sample in grams
P = % solids

10 Quality Control For Drinking Water Analysis

10.1 Minimum requirements

10.1.1 All quality control data should be maintained and available for easy reference or inspection.

10.1.2 An unknown performance sample (when available) must be analyzed once per year for the metals measured. Results must be within the control limit established by EPA. If problems arise, they should be corrected, and a follow-up performance sample should be analyzed.

10.2 Minimum Daily control

10.2.1 After a calibration curve composed of a minimum of a reagent blank and three standards has been prepared, subsequent calibration curves must be verified by use of at least a reagent blank and one standard at or near the MCL. Daily checks must be within ±10 percent of original curve.

10.2.2 If 20 or more samples per day are analyzed, the working standard curve must be verified by running an additional standard at or near the MCL every 20 samples. Checks must be within ±10 percent of original curve.

10.3 Optional Requirements

10.3.1 A current service contract should be in effect on balances and the atomic absorption spectrophotometer.

10.3.2 Class S weights should be available to make periodic checks on balances.

10.3.3 Chemicals should be dated upon receipt of shipment and replaced as needed or before shelf life has been exceeded.

10.3.4 A known reference sample (when available) should be analyzed once per quarter for the metals measured. The measured value should be within the control limits established by EPA.

10.3.5 At least one duplicate sample should be run every 10 samples, or with each set of samples to verify precision of the method. Checks should be within the control limit established by EPA.

10.3.6 Standard deviation should be obtained and documented for all measurements being conducted.

10.3.7 Quality Control charts or a tabulation of mean and standard deviation should be used to document validity of data on a daily basis.

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes—Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interference are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps *must* be taken to correct for potential interference effects. (See 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 Dissolved — Those elements which will pass through a 0.45 μm membrane filter.

3.2 Suspended — Those elements which are retained by a 0.45 μm membrane filter.

3.3 Total — The concentration determined on an unfiltered sample following vigorous digestion (9.3), or the sum of the dissolved plus suspended concentrations. (9.1 plus 9.2.)

3.4 Total recoverable — The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (9.4).

3.5 Instrumental detection limit — The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 Sensitivity — The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 Instrument check standard — A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

3.8 Interference check sample — A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2)

3.9 Quality control sample — A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.6.3)

3.10 Calibration standards — a series of know standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4)

3.11 Linear dynamic range — The concentration range over which the analytical curve remains linear.

3.12 Reagent blank — A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 7.5.2)

3.13 Calibration blank — A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 7.5.1)

3.14 Method of standard addition — The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 10.6.1)

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (14.7, 14.8 and 14.9) for the information of the analyst.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 Spectral interferences can be categorized as 1) overlap of a spectral line from another element; 2) unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination phenomena; and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multielement instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

The interference information, which was collected at the Ames Laboratory,[1] is expressed at analyte concentration eqivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system.

Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the

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[1] Ames Laboratory, USDOE, Iowa State University, Ames Iowa 50011

analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766 491 nm.

5.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aersol flow-rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

5.1.3 Chemical Interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

5.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 5.2.1 through 5.2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values.

5.2.1 Serial dilution—If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 % of the original determination (or within some acceptable control limit (14.3) that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

5.2.2 Spike addition—The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect. *Caution:* The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended. (See 5.2.3)

5.2.3 Comparison with alternate method of analysis—When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

5.2.4 Wavelength scanning of analyte line region—If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

6. Apparatus

6.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

6.1.1 Computer controlled atomic emission spectrometer with background correction.

6.1.2 Radiofrequency generator.

6.1.3 Argon gas supply, welding grade or better.

6.2 Operating conditions — Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

7. Reagents and standards

7.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

7.1.1 Acetic acid, conc. (sp gr 1.06).

7.1.2 Hydrochloric acid, conc. (sp gr 1.19).

7.1.3 Hydrochloric acid, (1+1): Add 500 mL conc. HCl (sp gr 1.19) to 400 mL deionized, distilled water and dilute to 1 liter.

7.1.4 Nitric acid, conc. (sp gr 1.41).

7.1.5 Nitric acid,(1+1): Add 500 mL conc. HNO_3 (sp. gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

7.2 *Dionized, distilled water:* Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (14.6).

7.3 *Standard stock solutions* may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 h at 105°C unless otherwise specified. (CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow:

7.3.1 Aluminum solution, stock, 1 mL = 100 μg Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.2 Antimony solution stock, 1 mL = 100 μg Sb: Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

7.3.3 *Arsenic solution, stock,* 1 mL = 100 µg As: Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.4 *Barium solution, stock,* 1 mL = 100 µg Ba: Dissolve 0.1516 g $BaCl_2$ (dried at 250°C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.5 *Beryllium solution, stock,* 1 mL = 100 µg Be: *Do not dry.* Dissolve 1.966 g $BeSO_4 \cdot 4\ 4H_2O$, in deionized, distilled water, add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.6 *Boron solution, stock,* 1 mL = 100 µg B: *Do not dry.* Dissolve 0.5716 g anhydrous H_3BO_3 in deionized distilled water dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

7.3.7 *Cadmium solution, stock,* 1 mL = 100 µg Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.8 *Calcium solution, stock,* 1 mL = 100 µg Ca: Suspend 0.2498 g $CaCO_3$ dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.9 *Chromium solution, stock,* 1 mL = 100 µg Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete, acidify with 10 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.10 *Cobalt solution, stock,* 1 mL = 100 µg Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.11 *Copper solution, stock,* 1 mL = 100 µg Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.12 *Iron solution, stock,* 1 mL = 100 µg Fe: Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO_3. Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.13 *Lead solution, stock,* 1 mL = 100 µg Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.14 *Magnesium solution, stock,* 1 mL = 100 µg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.15 *Manganese solution, stock,* 1 mL = 100 µg Mn: Dissolve 0.1000 g of manganese metal in the acid mixture 10 mL conc. HCl and 1 mL conc. HNO_3, and dilute to 1,000 mL with deionized, distilled water.

7.3.16 *Molybdenum solution, stock,* 1 mL = 100 µg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1,000 mL.

7.3.17 *Nickel solution, stock,* 1 mL = 100 µg Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3, cool and dilute to 1,000 mL with deionized, distilled water.

7.3.18 *Potassium solution, stock,* 1 mL = 100 µg K: Dissolve 0.1907 g KCl, dried at 110°C, in deionized, distilled water dilute to 1,000 mL.

7.3.19 *Selenium solution, stock,* 1 mL = 100 µg Se: *Do not dry.* Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.

7.3.20 *Silica solution, stock,* 1 mL = 100 µg SiO_2: *Do not dry.* Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.21 *Silver solution, stock,* 1 mL = 100 µg Ag: Dissolve 0.1575 g $AgNO_3$ in 100 mL of deionized, distilled water and 10 mL conc. HNO_3. Dilute to 1,000 mL with deionized, distilled water.

7.3.22 *Sodium solution, stock,* 1 mL = 100 µg Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.23 *Thallium solution, stock,* 1 mL = 100 µg Tl: Dissolve 0.1303 g $TlNO_3$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.24 *Vanadium solution, stock,* 1 mL = 100 µg V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.25 *Zinc solution, stock,* 1 mL = 100 µg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.4 *Mixed calibration standard solutions*—Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 7.4.1 thru 7.4.5) Add 2 mL of (1+1) HCl and dilute to 100 mL with deionized, distilled water. (See Notes 1 and 6.) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (See 7.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

7.4.1 *Mixed standard solution I*—Manganese, beryllium, cadmium, lead, and zinc.

7.4.2 *Mixed standard solution II*—Barium, copper, iron, vanadium, and cobalt.

7.4.3 *Mixed standard solution III*—Molybdenum, silica, arsenic, and selenium.

7.4.4 *Mixed standard solution IV*—Calcium, sodium, potassium, aluminum, chromium and nickel.

7.4.5 Mixed standard solution V—Antimony, boron, magnesium, silver, and thallium.

NOTE 1: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

7.5 Two types of blanks are required for the analysis. The calibration blank (3.13) is used in establishing the analytical curve while the reagent blank (3.12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

7.5.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. (See Note 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.

7.5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7.6 In addition to the calibration standards, an instrument check standard (3.7), an interference check sample (3.8) and a quality control sample (3.9) are also required for the analyses.

7.6.1 The *instrument check standard* is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. (See 12.1.1)

7.6.2 The *interference check sample* is prepared by the analyst in the following manner. Select a representative sample which contains minimal concentrations of the analytes of interest by known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 μg/L or 5 times the estimated detection limits given in Table 1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample will be available from the Quality Assurance Branch of EMSL-Cincinnati. (See 12.1.2)

7.6.3 The *quality control sample* should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/L and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured. (See 12.1.3)

8. Sample handling an preservation

8.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polyproplyene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order (See Notes 2 and 3).

NOTE 2: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chomic acid should not be used with plastic bottles.

NOTE 3: If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

8.2 Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

8.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 mL of (1+1) acid per liter should be sufficient to preserve the sample.

8.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

8.2.3 For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferable at the time of collection. The sample is not filtered before processing.

9. Sample Preparation

9.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. (See Note 6.) If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described in 9.3.

9.2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150-mL Griffin beaker and add 4 mL conc. HNO_3. Cover the beaker with a watch glass and heat gently. The wam acid will soon dissolve the membrane.

Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of conc. HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (2 mL), cool, add 10 mL HCl (1+1) and 15 mL deionized, distilled water per 100 mL dilution and warm the beaker gently for 15 min. to dissolve any precipitated or residue material. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined (See Note 6). The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

NOTE 4: In place of filtering, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

9.3 For the determination of total elements, choose a measured, volume of the well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 3 mL of conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5 mL portion of conc. HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness and cool the beaker. Add 10 mL of 1+1 HCl and 15 mL of deionized, distilled water per 100 mL of final solution and warm the beaker gently for 15 min. to dissolve any precipitate or residue resulting from evaporation. Allow to cool, wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis (See Note 6). Concentrations so determined shall be reported as "total."

NOTE 5: If low determinations of boron are critical, quartz glassware should be use.

NOTE 6: If the sample analysis solution has a different acid concentration from that given in 9.4, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

9.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume to 100 mL and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

10. Procedure

10.1 Set up instrument with proper operating parameters established in 6.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

10.2 Initiate appropriate operating configuration of computer.

10.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in 7.4. Flush the system with the calibration blank (7.5.1) between each standard. (See Note 7.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE 7: For boron concentrations greater than 500 µg/L extended flush times of 1 to 2 min. may be required.

10.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ± 5 percent (or the established control limits whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

10.5 Begin the sample run flushing the system with the calibration blank solution (7.5.1) between each sample. (See Note 7.) Analyze the instrument check standard (7.6.1) and the calibration blank (7.5.1) each 10 samples.

10.6 If it has been found that method of standard addition are required, the following procedure is recommended.

10.6.1 The standard addition technique (14.2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$c_X = \frac{S_B V_S c_S}{(S_A - S_B)\, V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and c_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus c_S is much greater than c_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same as the analyte in the sample.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

11. Calculation

11.1 Reagent blanks (7.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

11.2 If dilutions were performed, the appropriate factor must be applied to sample values.

11.3 Data should be rounded to the thousandth place and all results should be reported in mg/L up to three significant figures.

12. Quality Control (Instrumental)

12.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow:

12.1.1 Analyze an appropriate instrument check standard (7.6.1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within ±5% of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Analyze the calibration blank (7.5.1) at a frequency of 10%. The result should be within the established control limits of two standard deviations of the mean value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.2 To verify interelement and background correction factors analyze the interference check sample (7.6.2) at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.3 A quality control sample (7.6.3) obtained from an outside source must first be used for the initial verification of the calibration standards. A fresh dilution of this sample shall be anlayzed every week thereafter to monitor their stability. If the results are not within ±5% of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

Precision and Accuracy

13.1 In an EPA round robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 4 lists the true value, the mean reported value and the mean % relative standard deviation.

References

1. Winge, R.K., V.J. Peterson, and V.A. Fassel, "Inductively Coupled Plasma-Atomic Emission Spectroscopy: Prominent Lines," EPA-600/4-79-017.

2. Winefordner, J.D., "Trace Analysis: Spectroscopic Methods for Elements," *Chemical Analysis*, Vol. *46*, pp. 41-42.

3. Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019.

4. Garbarino, J.R. and Taylor, H.E., "An Inductively-Coupled Plasma Atomic Emission Spectrometric Method for Routine Water Quality Testing," Applied Spectroscopy *33*, No. 3(1979).

5. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.

6. Annual Book of ASTM Standards, Part 31.

7. "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977.

8. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

9. "Safety in Academic Chemistry Laboratories, American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

Table 1. Recommended Wavelengths[1] and Estimated Instrumental Detection Limits

Element	Wavelength, nm	Estimated detection limit, μg/L[2]
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	see[3]
Selenium	196.026	75
Silica (SiO_2)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[1] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 5.1.1.).

[2] The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines, "EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[3] Highly dependent on operating conditions and plasma position.

Table 2. *Analyte Concentration Equivalents (mg/L) Arising From Interferents at the 100 mg/L Level*

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	—	—	—	—	—	—	0.21	—	—	1.4
Antimony	206.833	0.47	—	2.9	—	0.08	—	—	—	.25	0.45
Arsenic	193.696	1.3	—	0.44	—	—	—	—	—	—	1.1
Barium	455.403	—	—	—	—	—	—	—	—	—	—
Beryllium	313.042	—	—	—	—	—	—	—	—	0.04	0.05
Boron	249.773	0.04	—	—	—	0.32	—	—	—	—	—
Cadmium	226.502	—	—	—	—	0.03	—	—	0.02	—	—
Calcium	317.933	—	—	0.08	—	0.01	0.01	0.04	—	0.03	0.03
Chromium	267.716	—	—	—	—	0.003	—	0.04	—	—	0.04
Cobalt	228.616	—	—	0.03	—	0.005	—	—	0.03	0.15	—
Copper	324.754	—	—	—	—	0.003	—	—	—	0.05	0.02
Iron	259.940	—	—	—	—	—	—	0.12	—	—	—
Lead	220.353	0.17	—	—	—	—	—	—	—	—	—
Magnesium	279.079	—	0.02	0.11	—	0.13	—	0.25	—	0.07	0.12
Manganese	257.610	0.005	—	0.01	—	0.002	0.002	—	—	—	—
Molybdenum	202.030	0.05	—	—	—	0.03	—	—	—	—	—
Nickel	231.604	—	—	—	—	—	—	—	—	—	—
Selenium	196.026	0.23	—	—	—	0.09	—	—	—	—	—
Silicon	288.158	—	—	0.07	—	—	—	—	—	—	0.01
Sodium	588.995	—	—	—	—	—	—	—	—	0.08	—
Thallium	190.864	0.30	—	—	—	—	—	—	—	—	—
Vanadium	292.402	—	—	0.05	—	0.005	—	—	—	0.02	—
Zinc	213.856	—	—	—	0.14	—	—	—	0.29	—	—

Table 3. *Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table 2.*

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

Table 4. *ICP Precision and Accuracy Data*

Element	Sample # 1 True Value µg/L	Sample # 1 Mean Reported Value µg/L	Sample # 1 Mean Percent RSD	Sample #2 True Value µg/L	Sample #2 Mean Reported Value µg/L	Sample #2 Mean Percent RSD	Sample #3 True Value µg/L	Sample #3 Mean Reported Value µg/L	Sample #3 Mean Percent RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

Not all elements were analyzed by all laboratories.

ALUMINUM

Method 202.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01105
Dissolved 01106
Suspended 01107

Optimum Concentration Range: 5–50 mg/l using a wavelength of 309.3 nm
Sensitivity: 1 mg/l
Detection Limit: 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 gram of aluminum metal (analytical reagent grade). Add 15 ml of conc. HCl and 5 ml conc. HNO_3 to the metal, cover the beaker and warm gently. When solution is complete, transfer quantitatively to a 1 liter volumetric flask and make up to volume with deionized distilled water. 1 ml = 1 mg Al (1000 mg/l).
2. Potassium Chloride Solution: Dissolve 95 g potassium chloride (KCl) in deionized distilled water and make up to 1 liter.
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing. To each 100 ml of standard and sample alike add 2.0 ml potassium chloride solution.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for the preparation of the sample as given in part 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Aluminum hollow cathode lamp
2. Wavelength: 309.3 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide

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5. Type of flame: Fuel rich

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Interferences

1. Aluminum is partially ionized in the nitrous oxide-acetylene flame. This problem may be controlled by the addition of an alkali metal (potassium, 1000 *ug*/ml) to both sample and standard solutions.

Notes

1. The following lines may also be used:
   308.2 nm Relative Sensitivity 1
   396.2 nm Relative Sensitivity 2
   394.4 nm Relative Sensitivity 2.5
2. Data to be entered into **STORET** must be reported as *ug*/1.
3. For concentrations of aluminum below 0.3 mg/1, the furnace procedure (Method 202.2) is recommended.
4. The Eriochrome cyanine R colorimetric method may also be used. The optimum range for this method lies between 20 and 300 *ug*/1. (Standard Methods, 14th Edition, p. 171.) In the absence of fluorides and complex phosphates, a detection limit of 6 ug/1 is possible.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for aluminum were as follows:

Number of Labs	True values ug/liter	Mean Value ug/liter	Deviation ug/liter	Accuracy as %Bias
38	1205	1281	299	6.3
38	1004	1003	391	–0.1
37	500	463	202	–7.4
37	625	582	272	–6.8
22	35	96	108	175
21	15	109	168	626

ALUMINUM

Method 202.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01105
Dissolved 01106
Suspended 01107

Optimum Concentration Range: 20–200 ug/1
Detection Limit: 3 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1300°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmmosphere: Argon
5. Wavelength: 309.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the caculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Issued 1978

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 *ul* injection, continuous flow purge gas and non-pyrolytic graphite.
2. Background correction may be required if the sample contains high dissolved solids.
3. It has been reported that chloride ion and that nitrogen used as a purge gas suppress the aluminum signal. Therefore the use of halide acids and nitrogen as a purge gas should be avoided.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

ANTIMONY

Method 204.1 (Atomic absorption, direct aspiration)

STORET NO. Total 01097
Dissolved 01095
Suspended 01096

Optimum Concentration Range: 1–40 mg/l using a wavelength of 217.6 nm
Sensitivity: 0.5 mg/l
Detection Limit: 0.2 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.7426 g of antimony potassium tartrate $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$ (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Sb (1000 mg//l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Antimony hollow cathode lamp
2. Wavelength: 217.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Fuel lean

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Interferences

1. In the presence of lead (1000 mg/1), a spectral interference may occur at the 217.6 nm resonance line. In this case the 231.1 nm antimony line should be used.
2. Increasing acid concentrations decrease antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards should be matched.

Notes

1. Data to be entered into **STORET** must be reported as ug/1.
2. For concentrations of antimony below 0.35 mg/1, the furnace procedure (Method 204.2) is recommended.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 5.0 and 15 mg Sb/1, the standard deviations were ±0.08 and ±0.1, respectively. Recoveries at these levels were 96% and 97%, respectively.

ANTIMONY

Method 204.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01097
Dissolved 01095
Suspended 01096

Optimum Concentration Range: 20–300 ug/1
Detection Limit: 3 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.2% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.3 of the Atomic Absorption Methods section of this manual should be followed including the addition of sufficient 1:1 HCl to dissolve the digested residue for the analysis of suspended or total antimony. The sample solutions used for analysis should contain 2% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–800°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 217.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess of 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as *ug/1*.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

ARSENIC

Method 206.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01002
Dissolved 01000
Suspended 01001

Optimum Concentration Range: 5–100 ug/1
Detection Limit: 1 ug/1

Preparation of Standard Solution

1. Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 ml of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter. 1 ml = 1 mg As (1000 mg/1).

2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100ml.

3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.

4. Working Arsenic Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2ml of 30% H_2O_2 and 2ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.

2. Cool and bring back to 50 ml with deionized distilled water.

3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace.

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NOTE: If solubilization or digestion is not required, adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30%H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1100°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 193.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
4. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent containing 15 *ug*/1 and spiked with concentrations of 2, 10 and 25 *ug*/1, recoveries of 85%, 90% and 88% were obtained respectively. The relative standard deviation at these concentrations levels were ±8.8%, ±8.2%, ±5.4% and ±8.7%, respectively.
2. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 20, 50 and 100 *ug* As/1, the standard deviations were ±0.7, ±1.1 and ±1.6 respectively. Recoveries at these levels were 105%, 106% and 101%, respectively.

ARSENIC

Method 206.3 (Atomic Absorption—gaseous hydride)

STORET NO. Total 01002
Dissolved 01000
Suspended 01001

1. Scope and Application

1.1 The gaseous hydride method determines inorganic arsenic when present in concentrations at or above 2 *ug*/l. The method is applicable to drinking water and most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel and silver.

2. Summary of Method

2.1 Arsenic in the sample is first reduced to the trivalent form using $SnCl_2$ and converted to arsine, AsH_3, using zinc metal. The gaseous hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the method is 2–20 *ug*/l. The 193.7 nm wavelength line is used.

3. Comments

3.1 In analyzing drinking water and most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of arsenic to establish adequate recovery.

3.2 Organic forms of arsenic must be converted to inorganic compounds and organic matter must be oxidized before beginning the analysis. The oxidation procedure given in Method 206.5 (Standard Methods, 14th Edition, Method 404B, p. 285, Procedure 4.a) has been found suitable.

3.3 For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

3.4 For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.

3.5 Data to be entered into **STORET** must be reported as *ug*/l.

4. Precision and Accuracy

4.1 Ten replicate solutions of o-arsenilic acid at the 5, 10 and 20 *ug*/l level were analyzed by a single laboratory. Standard deviations were ±0.3, ±0.9 and ±1.1 with recoveries of 94, 93 and 85%, respectively. (Caldwell, J. S., Lishka, R. J., and McFarren, E. F., "Evaluation of a Low Cost Arsenic and Selenium Determination at Microgram per Liter Levels", JAWWA., vol 65, p 731, Nov., 1973.)

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5. References

5.1. Except for the perchloric acid step, the procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 14th Edition, p159, Method 301A(VII),(1975)

ARSENIC

Method 206.4 (Spectrophotometric-SDDC)

STORET NO. 01002
Inorganic, Dissolved 00095
Inorganic, Total 00997
Inorganic, Suspended 00996

1. Scope and Application
   1.1 The silver diethyldithiocarbamate method determines inorganic arsenic when present in concentrations at or above 10 ug/1. The method is applicable to drinking water and most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver. Domestic and industrial wastes may also be analyzed after digestion (see 3.3).
   1.2 Difficulties may be encountered with certain industrial waste materials containing volatile substances. High sulfur content of wastes may exceed removal capacity of the lead acetate scrubber.
2. Summary of Method
   2.1 Arsenic in the sample is reduced to arsine, AsH_3, in acid solution in a hydrogen generator. The arsine is passed through a scrubber to remove sulfide and is absorbed in a solution of silver diethyldithiocarbamate dissolved in pyridine. The red complex thus formed is measured in a spectrophotometer at 535 nm.
3. Comments
   3.1 In analyzing drinking water and most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of arsenic to establish adequate recovery.
   3.2 It is essential that the system be airtight during evolution of the arsine, to avoid losses.
   3.3 If concentration of the sample and/or oxidation of any organic matter is required, refer to Method 206.5. [Standard Methods, 14th Edition, Method 404B, p. 284, Procedure 4.a (1975)]. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.
      3.3.1 Since nitric acid gives a negative interference in this test, use sulfuric acid as a preservative if only inorganic arsenic is being measured.
   3.4 1-Ephedrine in chloroform has been found to be a suitable solvent for silver diethyldithiocarbamate if the analyst finds the odor of pyridine objectionable [Anal. Chem. 45, 1786 (1973)].
   3.5 For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.

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4. Precision and Accuracy

4.1 In a round-robin study reported by Standard Methods a synthetic unknown sample containing 40 ug/1, as As, with other metals was analyzed in 46 laboratories. Relative standard deviation was ±13.8% and relative error was 0%.

5. Reference

5.1 The procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 283, Method 404A (1975).

ARSENIC

Method 206.5 (Sample Digestion Prior to Total Arsenic Analysis by Silver Diethyldithiocarbamate or Hydride Procedures)

1. Scope and Application:

   1.1 Both the silver diethyldithiocarbamate spectrophotometric method and the AA hydride procedure measure inorganic arsenic. Therefore, if either of these procedures are being employed for the purpose of measuring total arsenic (inorganic plus organic), all organically bound arsenic must first be converted to an inorganic form prior to the analytical determination. This may be accomplished with H_2SO_4–HNO_3.

2. Procedure

   2.1 To a suitable sample containing from 2 to 30 *u*g of arsenic, add 7 ml (1 + 1) H_2SO_4 and 5 ml conc HNO_3. Evaporate the sample to SO_3 fumes. Caution: If the sample chars, stop the digestion immediately, cool and add additional conc HNO_3. Continue digestion adding additional conc HNO_3 as necessary.

   2.2 If the sample remains colorless, or straw-yellow during evolution of SO_3 fumes, the digestion is complete.

   2.3 Cool the digested sample, add about 25 ml distilled water, and again evaporate to SO_3 fumes to expel oxides of nitrogen.

   2.4 The sample is now ready for analysis using either the hydride or spectrophotometric procedure.

3. Interferences

   3.1 All traces of nitric acid must be removed before either the spectrophotometric or the hydride procedures are applied. Oxides of nitrogen should be expelled by taking the sample to fumes of SO_3.

4. Notes

   4.1 The digestion step may be carried out in a flask on a hot-plate or in a Kjeldahl apparatus. This digestion step may also be used, in effect, to concentrate the sample, inasmuch as any size volume may be processed.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, p285, method 404B, step 4a, 14th Edition (1975).

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BARIUM

Method 208.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01007
Dissolved 01005
Suspended 01006

Optimum Concentration Range: 1–20 mg/1 using a wavelength of 553.6 nm
Sensitivity: 0.4 mg/1
Detection Limit: 0.1 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7787 g barium chloride ($BaCl_2 \cdot 2H_2O$, analytical reagent grade) in deionized distilled water and dilute to 1 liter. 1 ml = 1 mg Ba (1000 mg/1).
2. Potassium chloride solution: Dissolve 95 g potassium chloride, KCl, in deionized distilled water and make up to 1 liter.
3. Prepare dilutions of the stock barium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike add 2.0 ml potassium chloride solution. The calibration standards should be prepared using the same type of acid and the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Barium hollow cathode lamp
2. Wavelength: 553.6 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

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Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Interferences

1. The use of a nitrous oxide-acetylene flame virtually eliminates chemical interference; however, barium is easily ionized in this flame and potassium must be added (1000 mg/1) to standards and samples alike to control this effect.
2. If the nitrous oxide flame is not available and acetylene-air is used, phosphate, silicon and aluminum will severely depress the barium absorbance. This may be overcome by the addition of 2000 mg/1 lanthanum.

Notes

1. Data to be entered into **STORET** must be reported as *ug*/1.
2. For concentrations of barium below 0.2 mg/1, the furnace procedure (Method 208.2) is recommended.
3. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.40 and 2.0 mg Ba/1, the standard deviations were ±0.043 and ±0.13, respectively. Recovereis at these levels were 94% and 113%, respectively.
2. In a round-robin study reported by Standard Methods (13th Edition, p215, method 129A, 1971), three synthetic samples containing barium were analyzed by 13 laboratories. At concentrations of 500, 1000 and 5000 *ug* Ba/1, the reported standard deviations were ±50, ±89 and ±185 *ug*, respectively. The relative error at these concentrations was 8.6%, 2.7% and 1.4%, respectively.

BARIUM

Method 208.2 (Atomic Absorption, furnace technique)

STORET NO. 01007
Dissolved 01005
Suspended 01006

Optimum Concentration Range: 10–200 *ug/l*
Detection Limit: 2 *ug/l*

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1200°C.
3. Atomizing Time and Temp: 10 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 553.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite.

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2. The use of halide acid should be avoided.
3. Because of possible chemical interaction, nitrogen should not be used as a purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 500 and 1000 *ug* Ba/1, the standard deviations were ±2.5 and ±2.2 *ug*, respectively. Recoveries at these levels were 96% and 102%, respectively A dilution of 1:10 was required to bring the spikes within the analytical range of the method.

BERYLLIUM

Methods 210.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01012
Dissolved 01010
Suspended 01011

Optimum Concentration Range: 0.05–2 mg/1 using a wavelength of 234.9 nm
Sensitivity: 0.025 mg/1
Detection Limit: 0.005 mg/1

Preparation of Standard Solution

1. Stock solution: Dissolve 19.6558 g beryllium sulfate, $BeSO{\bullet}4H_2O$, in deionized distilled water containing 2 ml conc. nitric acid and dilute to 1 liter. 1 ml = 1 mg Be (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Beryllium hollow cathode lamp
2. Wavelength: 234.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Interferences

1. Sodium and silicon at concentrations in excess of 1000 mg/1 have been found to severely depress the beryllium absorbance.
2. Bicarbonate ion is reported to interfere; however, its effect is eliminated when samples are acidified to a pH of 1.5.
3. Aluminum at concentrations of 500 *ug*/1 is reported to depress the sensitivity of beryllium [Spectrochim Acta 22, 1325 (1966)].

Notes

1. Data to be entered into **STORET** must be reported as *ug*/1.
2. The "aluminon colorimetric method" may also be used (Standard Methods, 14th Edition, p 177). The minimum detectable concentration by this method is 5 *ug*/1.
3. For concentrations of beryllium below 0.02 mg/1, the furnace procedure (Method 210.2) is recommended.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.01, 0.05 and 0.25 mg Be/1, the standard deviations were ±0.001, ±0.001 and ±0.002, respectively. Recoveries at these levels were 100%, 98% and 97%, respectively.

BERYLLIUM

Method 210.2 (Atomic Absorption, furnace technique)

STORET NO. 01012
Dissolved 01010
Suspended 01011

Optimum Concentration Range: 1–30 ug/1
Detection Limit: 0.2 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1000°C.
3. Atomizing Time and Temp: 10 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 234.9 nm
6. The operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation see "Furnace Procedure" part 9.3 of the Atomic Absorption methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can

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be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Because of possible chemical interaction and reported lower sensitivity, nitrogen should not be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and Accuracy data are not available at this time.

BORON

Method 212.3 (Colorimetric, Curcumin)

STORET NO. Total 01022
Dissolved 01020
Suspended 01021

1. Scope and Application
   1.1 This colorimetric method finds maximum utility for waters whose boron content is below 1 mg/1.
   1.2 The optimum range of the method on undiluted or unconcentrated samples is 0.1–1.0 mg/1 of boron.
   1.3 This method is applicable to drinking, and surface waters, domestic and industrial wastes.
2. Summary of Method
   2.1 When a sample of water containing boron is acidified and evaporated in the presence of curcumin, a red-colored product called rosocyanine is formed. The rosocyanine is taken up in a suitable solvent, and the red color is compared with standards photometrically.
3. Comments
   3.1 Nitrate nitrogen concentrations above 20 mg/1 interfere.
   3.2 Significantly high results are possible when the total of calcium and magnesium hardness exceeds 100 mg/1 as $CaCO_3$. Passing the sample through a cation exchange resin eliminates this problem.
   3.3 Close control of such variables as volumes and concentrations of reagents, as well as time and temperature of drying, must be exercised for maximum accuracy.
   3.4 Data to be entered into STORET must be reported as *ug*/1.
4. Precision and Accuracy
   4.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 240 *ug*/1 B, 40 *ug*/1 As, 250 *ug*/1 Be, 20 *ug*/1 Se, and 6 *ug*/1 V in distilled water, was analyzed by the curcumin method with a relative standard deviation of 22.8% and a relative error of 0% in 30 laboratories.
5. Reference
   5.1 The procedure to be used for this determination is found in:
   Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 287, Method 405A (1975).

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CADMIUM

Method 213.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01027
Dissolved 01025
Suspended 01026

Optimum Concentration Range: 0.05–2 mg/1 using a wavelength of 228.8 nm
Sensitivity: 0.025 mg/1
Detection Limit: 0.005 mg/1

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.282 g of cadmium sulfate ($3CdSO_4 \cdot 8H_2O$, analytical reagent grade) and dissolve in deionized distilled water make up to 1 liter with deionized distilled water. 1 ml = 1 mg Cd (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Cadmium hollow cathode lamp
2. Wavelength: 228.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. For levels of cadmium below 20 *ug*/1, either the Special Extraction Procedure given in Part 9.2 of the Atomic Absorption methods section as the furnace technique, Method 213.2 is recommended.
2. Data to be entered into **STORET** must be reported as *ug*/1.
3. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for cadmium were as follows:

Number of Labs	True Values *ug*/liter	Mean Value *ug*/liter	Standard Deviation *ug*/liter	Accuracy as % Bias
74	71	70	21	-2.2
73	78	74	18	-5.7
63	14	16.8	11.0	19.8
68	18	18.3	10.3	1.9
55	1.4	3.3	5.0	135
51	2.8	2.9	2.8	4.7

CADMIUM

Method 213.2 (Atomic Absorption, furnace technique)

STORET NO. 01027
Dissolved 01025
Suspended 01026

Optimum Concentration Range: 0.5–10 ug/l
Detection Limit: 0.1 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Ammonium Phosphate solution (40%): Dissolve 40 grams of ammonium phosphate, $(NH_4)_2HPO_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml.
3. Prepare dilutions of the stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike add 2.0 ml of the ammonium phosphate solution. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–500°C.
3. Atomizing Time and Temp: 10 sec–1900°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 228.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Contamination from the work area is critical in cadmium analysis. Use of pipet tips which are free of cadmium is of particular importance. (See part 5.2.9 of the Atomic Absorption Methods section of this manual.)
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 2.5, 5.0 and 10.0 *ug* Cd/1, the standard deviations were ±0.10, ±0.16 and ±0.33, respectively. Recoveries at these levels were 96%, 99% and 98%, respectively.

CALCIUM

Method 215.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 00916
Dissolved 00915

Optimum Concentration Range: 0.2–7 mg/1 using a wavelength of 422.7 nm
Sensitivity: 0.08 mg/1
Detection Limit: 0.01 mg/1

Preparation of Standard Solution

1. Stock Solution: Suspend 1.250 g of $CaCO_3$ (analytical reagent grade), dried at 180°C for 1 hour before weighing, in deionized distilled water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1000 ml with deionized distilled water. 1 ml = 0.5 mg Ca (500 mg/1).
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions, in 250 ml conc. HCl (Caution: Reaction is violent) and dilute to 500 ml with deionized distilled water.
3. Prepare dilutions of the stock calcium solutions to be used as calibration standards at the time of analysis. To each 10 ml volume of calibration standard and sample alike add 1.0 ml of the lanthanum chloride solution, i.e., 20 ml of standard or sample + 2 ml $LaCl_3$ = 22 ml.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. For the analysis of total calcium in domestic and industrial effluents, the procedures for the determination of total metals as given in parts 4.1.3 and 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.
2. For ambient waters, a representative aliquot of a well-mixed sample may be used directly for analysis. If suspended solids are present in sufficient amounts to clog the nebulizer, the sample may be allowed to settle and the supernatant liquid analyzed directly.

Instrumental Parameters (General)

1. Calcium hollow cathode lamp
2. Wavelength: 422.7 nm

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3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Reducing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Since low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1000 mg/1 also cause low calcium values. Concentrations of up to 500 mg/1 each of sodium, potassium and nitrate cause no interference.
2. Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.
3. The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame. (Atomic Absorption Newsletter 14, 29 [1975]).
4. The 239.9 nm line may also be used. This line has a relative sensitivity of 120.
5. Data to be entered into **STORET** must be reported as mg/1.
6. The EDTA titrimetric method may also be used (Standard Methods, 14th Edition, p 189).

Precision and Accuracy

1. In a single laboratory (EMSL), using distilled water spiked at concentrations of 9.0 and 36 mgCa/1, the standard deviations were ±0.3 and ±0.6, respectively. Recoveries at both these levels were 99%.

CALCIUM

Method 215.2 (Titrimetric, EDTA)

STORET NO. Calcium (mg/1 $CaCO_3$) 00910
Calcium, Total (mg/1 Ca) 00916

1. Scope and Application
   1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.
   1.2 The lower detection limit of this method is approximately 0.5 mg/1 as $CaCO_3$; the upper limit can be extended to all concentrations by sample dilution. It is recommended that a sample aliquot containing not more than 25 mg $CaCO_3$ be used.
2. Summary of Method
   2.1 Calcium ion is sequestered upon the addition of disodium dihydrogen ethylenediamine tetraacetate (EDTA). The titration end point is detected by means of an indicator which combines with calcium only.
3. Interferences
   3.1 Strontium and barium interfere and alkalinity in excess of 30 mg/1 may cause an indistinct end point. Magnesium interference is reduced or eliminated by raising the pH between 12–13 to precipitate magnesium hydroxide.
4. Apparatus
   4.1 Routine laboratory titrimetric glassware
5. Reagents
   5.1 Sodium hydroxide, NaOH, 1 N
   5.2 Indicators
      5.2.1 Many indicators are available, both laboratory prepared and commercial, and may be used. Two are described here.
      5.2.2 Murexide (ammonium purpurate) indicator: This changes from pink to purple. Dissolve 150 mg of the dye in 100 g absolute ethylene glycol. If a dry powder is preferred mix 200 mg murexide with 100 g solid NaCl and grind to 40 to 50 mesh. Titrate immediately after adding indicator because it is unstable under alkaline conditions.
      5.2.3 Eriochrome Blue Black R (sodium-1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid) indicator: This changes from red through purple to bluish purple to a pure blue without any trace of red or purple tint. The pH of some waters must be raised to 14 (rather than 12–13) by the use of 8 N NaOH in order to get a good color change. Grind in a mortar 200 mg powdered dye and 100 g solid NaCl to 40 to 50 mesh. Store in tightly stoppered bottle. Use 0.2 g of this mixture for titration.

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5.3 Standard EDTA titrant, 0.02 N: Place 3.723 g analytical reagent grade disodium ethylenediamine tetraacetate dihydrate, $Na_2H_2C_{10}H_{12}O_8N_2 \cdot 2\ H_2O$ in a 1 liter volumetric flask and dilute to the mark with distilled water. Check with standard calcium solution (5.3.1) by titration (5.3.5). Store in polyethylene. Check periodically because of gradual deterioration.

5.3.1 Standard calcium solution, 0.02 N: Place 1.000 g anhydrous calcium carbonate (primary standard low in heavy metals, alkalies and magnesium) in a 500 ml flask. Add, a little at a time 1 + 1 HCl (5.3.2) until all of the $CaCO_3$ has dissolved. Add 200 ml distilled water. Boil for a few minutes to expel CO_2. Cool. Add a few drops of methyl red indicator (5.3.3) and adjust to intermediate orange color by adding 3N NH_4OH (5.3.4) or 1 + 1 HCl (5.3.2) as required. Quantitatively transfer to a 1 liter volumetric flask and dilute to mark with distilled water.

5.3.2 Hydrochloric acid solution, 1 + 1

5.3.3 Methyl red indicator: Dissolve 0.10 g methyl red in distilled water in a 100 ml. volumetric flask and dilute to mark.

5.3.4 Ammonium hydroxide solution, 3 N

5.3.5 Standardization titration procedure: Place 10 ml standard calcium solution (5.3.1) in a vessel containing about 50 ml distilled water. Add 1 ml buffer solution (5.3.6). Add 1-2 drops indicator (5.3.7) or small scoop of dry indicator (5.3.7). Titrate slowly with continuous stirring until the last reddish tinge disappears, adding last few drops at 3–5 second intervals. At end point the color is blue. Total titration duration should be ≤ 5 minutes from the time of buffer addition.

$$\text{N of EDTA} = \frac{0.2}{\text{ml EDTA}}$$

5.3.6 Buffer solution: Dissolve 16.9 g ammonium chloride in 143 ml conc ammonium hydroxide in a 250 ml volumetric flask. Add 1.25 g of magnesium salt of EDTA (5.3.8) and dilute to the mark with distilled water. Store in tightly stoppered plastic bottle.

5.3.7 Indicator: Commercially available Eriochrome Black T is used in one of the three methods described. All gradually deteriorate.

5.3.7.1 Mix 0.5 g dye with 4.5 g hydroxylamine hydrochloride. Dissolve in 100 ml of 95% ethanol or isopropanol.

5.3.7.2 Place 0.5–1.0 g dye in 100 g of triethanolamine or 2-methoxyethanol.

5.3.7.3 Mix 0.5 g dye and 100 g NaCl for dry formulation.

5.3.8 EDTA Magnesium Salt: Commercially available.

6. Procedure

6.1 Pretreatment

6.1.1 For drinking waters, surface waters, saline waters, and dilutions thereof, no pretreatment steps are necessary. Proceed to 6.2.

6.1.2 For most wastewaters and highly polluted waters, the sample must be digested as given in the Atomic Absorption Methods section of this manual, paragraphs 4.1.3 and 4.1.4. Following this digestion, proceed to 6.2.

6.2 Sample Preparation:

6.2.1 The calcium content of the 50 ml aliquot to be titrated should be 5–10 mg, therefore dilution should be used for high calcium concentrations.

6.2.2 If the alkalinity is > 300 mg/l $CaCO_3$ and cannot be reduced by dilution because of low calcium concentration, the alkalinity must be decreased by acidifying, boiling one minute and cooling.

6.3 Titration

6.3.1 Add 2.0 ml NaOH solution (5.1), or a volume sufficient to produce pH 12 to 13, to 50 ml of sample.

6.3.2 Stir. Add 0.1 to 0.2 g indicator (5.2.2 or 5.2.3) or 1–2 drops if indicator solution is used.

6.3.3 Immediately titrate with continuous stirring. Check to see that no further color change occurs when using murexide (5.2.2) by adding 1 to 2 more drops of titrant after recording milliliters of titrant at first judged end point.

7. Calculations

7.1 Total calcium

$$\text{mg/l Ca} = \frac{A \times N \times 20{,}040}{\text{ml of sample}}$$

where:

A = ml titrant

N = Normality of EDTA solution

7.2 Calcium hardness

$$\text{mg/l } CaCO_3 = \frac{A \times N \times 50{,}000}{\text{ml of sample}}$$

where A and N are the same as in 7.1.

8. Precision and Accuracy

8.1 A synthetic unknown sample containing 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 1.1 mg/l nitrate N, 250 ug/l nitrite N, 259 mg/l sulfate, and 42.5 mg/l total alkalinity in distilled water was determined by this method with a relative standard deviation of 9.2% and a relative error of 1.9% in 44 laboratories.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 189, Method 306C (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D511-76, Method B, p 253 (1976).

CHROMIUM

Method 218.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01034
Dissolved 01030
Suspended 01031

Optimum Concentration Range: 0.5–10 mg/l using a wavelength of 357.9 nm
Sensitivity: 0.25 mg/l
Detection Limit: 0.05 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.923 g of chromium trioxide (CrO_3, reagent grade) in deionized distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Cr (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Chromium hollow cathode lamp
2. Wavelength: 357.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. The following wavelengths may also be used:
   359.3 nm Relative Sensitivity 1.4
   425.4 nm Relative Sensitivity 2
   427.5 nm Relative Sensitivity 3
   428.9 nm Relative Sensitivity 4
2. The fuel rich air–acetylene flame provides greater sensitivity but is subject to chemical and matrix interference from iron, nickel, and other metals. If the analysis is performed in a lean flame the interference can be lessened but the sensitivity will also be reduced.
3. The suppression of both Cr (III) and Cr (VI) absorption by most interfering ions in fuel rich air-acetylene flames is reportedly controlled by the addition of 1% ammonium bifluoride in 0.2% sodium sulfate [Talanta 20, 631 (1973)]. A 1% oxine solution is also reported to be useful.
4. For levels of chromium between 50 and 200 *ug*/1 where the air-acetylene flame can not be used or for levels below 50 *ug*/1, either the furnace procedure or the extraction procedure is recommended. See Method 218.2 for the furnace procedure and Method 218.3 for the chelation–extraction procedure.
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into **STORET** must be reported as *ug*/1.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for chromium were as follows:

Number of Labs	True Values ug/liter	Mean Value ug/liter	Standard Deviation ug/liter	Accuracy as % Bias
74	370	353	105	–4.5
76	407	380	128	–6.5
72	74	72	29	–3.1
70	93	84	35	–10.2
47	7.4	10.2	7.8	37.7
47	15.0	16.0	9.0	6.8

CHROMIUM

Method 218.2 (Atomic Absorption, furnace technique)

STORET NO. 01034
Dissolved 01030
Suspended 01031

Optimum Concentration Range: 5–100 ug/1
Detection Limit: 1 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Calcium Nitrate Solution: Dissolve 11.8 grams of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml. 1 ml = 20 mg Ca.
3. Prepare dilutions of the stock chromium solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3. To each 100 ml of standard and sample alike, add 1 ml of 30% H_2O_2 and 1 ml of the calcium nitrate solution.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% v/v HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1000°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 357.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injecton, continuous flow purge gas and non-pyrolytic graphite.
2. Hydrogen peroxide is added to the acidified solution to convert all chromium to the trivalent state. Calcium is added to a level above 200 mg/1 where its suppressive effect becomes constant up to 1000 mg/1.
3. Background correction may be required if the sample contains high dissolved solids.
4. Nitrogen should not be used as a purge gas because of possible CN band interference.
5. Pipet tips have been reported to be a possible source of contamination. (See part 5.2.9 of the Atomic Absorption Methods section of this manual.)
6. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
7. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
8. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
9. Data to be entered into STORET must be reported as *u*g/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 19, 48, and 77 *u*g Cr/1, the standard deviations were ±0.1, ±0.2, and ±0.8, respectively. Recoveries at these levels were 97%, 101%, and 102%, respectively.

CHROMIUM

Method 218.3 (Atomic Absorption, chelation-extraction)

STORET NO. 01034

1. Scope and Application
   - 1.1 This method covers the determination of total chromium in drinking, surface and saline waters. The method may also be applicable to certain domestic and industrial wastes provided that no interfering substances are present. (See 3.1)
   - 1.2 The method may be used to analyze samples containing from 1.0 to 25 ug of chromium per liter.
   - 1.3 For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.
2. Summary of the Method
   - 2.1 This method is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) following oxidation of trivalent chromium. The chelate is extracted with methyl isobutyl ketone (MIBK) and aspirated into the flame of the atomic absorption spectrophotometer.
   - 2.2 Hexavalent chromium may also be chelated with pyrrolidine dithiocarbamic acid in chloroform as described in section 9.2 of the atomic absorption text found in this manual.
3. Interferences
   - 3.1 High concentrations of other reactive metals, as may be found in wastewaters, may interfere. The method is free from interferences from elements normally occurring in fresh water.
4. Instrumental Parameters (General)
   - 4.1 Chromium hollow cathode lamp.
   - 4.2 Wavelength: 357.9 nm
   - 4.3 Fuel: Acetylene
   - 4.4 Oxidant: Air
   - 4.5 Type of flame: Fuel rich (adjust for organic solvent).
5. Reagents
   - 5.1 Ammonium pyrrolidine dithiocarbamate (APDC) solution. Dissolve 1.0 g APDC in demineralized water and dilute to 100 ml. Prepare fresh daily.
   - 5.2 Bromophenol blue indicator solution: Dissolve 0.1 g bromophenol blue in 100 ml 50-percent ethanol.
   - 5.3 Potassium dichromate standard solution, 1.0 ml = 0.08 mg Cr: Dissolve 0.2263 g dried analytical reagent grade $K_2Cr_2O_7$ in demineralized water and make up to 1000 ml.
   - 5.4 Trivalent chromium stock solution, 1.0 ml = 0.002 mg $Cr^{+}3$: Pipet 5.00 ml of the potassium dichromate standard solution (5.3) into an Erlenmeyer flask. Add approximately 15 mg Na_2SO_3 and 0.5 ml concentrated HNO_3. Gently evaporate to

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dryness; strong heating reoxidizes the chromium. Add 0.5 ml concentrated HNO_3 and again evaporate to dryness to destroy any excess sulfite. Take up in 1 ml concentrated HNO_3 with warming and dilute to 200.0 ml with demineralized water.

5.5 Trivalent chromium working solution, 1.0 ml = 0.005 mg Cr^{+3}: Immediately before use, dilute 25.0 ml of trivalent chromium stock solution (5.4) to 100.0 ml with demineralized water.

5.6 Potassium permanganate, 0.1 N: Dissolve 0.32 g potassium permanganate in 100 ml demineralized water.

5.7 Sodium azide, 0.1%: Dissolve 100 mg sodium azide in demineralized water and dilute to 100 ml.

5.8 Methyl isobutyl ketone (MIBK).

5.9 Sodium hydroxide solution, 1 M: Dissolve 40 g NaOH in demineralized water and dilute to 1 liter.

5.10 Sulfuric acid, 0.12 M: Slowly add 6.5 ml concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 liter.

6. Procedure

6.1 Pipet a volume of sample containig less than 2.5 ug chromium (100 ml maximum) into a 200 ml volumetric flask, and adjust the volume to approximately 100 ml. The pH must be 2.0 or less. Add concentrated HNO_3 if necessary.

6.2 Acidify a liter of demineralized water with 1.5 ml concentrated HNO_3. Prepare a blank and sufficient standards using trivalent chromium and adjust volumes to approximately 100 ml with the acidified demineralized water.

6.3 Add 0.1 N $KMnO_4$ dropwise to both standards and samples until a faint pink color persists.

6.4 Heat on a steam bath for 20 minutes. If the color disappears, add additional $KMnO_4$ solution dropwise to maintain a slight excess.

6.5 While still on the steam bath, add sodium azide solution dropwise until the $KMnO_4$ color just disappears. Heat for about 2 min between each addition and avoid adding any excess. Continue heating for 5 min after adding the last drop of sodium azide solution.

6.6 Transfer the flasks to a water bath and cool to room temperature.

6.7 Remove from the water bath and filter (through Whatman No. 40 filter paper or equivalent) any sample which has a brownish precipitate or coloration which may interfere with the pH adjustment.

6.8 Add 2 .0 ml of 1 M NaOH and 2 drops bromophenol blue indicator solution. Continue the addition of 1 M NaOH dropwise to all samples and standards in which the indicator change from yellow to blue has not occurred. Add 0.12 M H_2SO_4 dropwise until the blue color just disappears, then add 2.0 ml in excess. The pH at this point will be 2.4.

6.9 The pH adjustment to 2.4 may also be made with a pH meter instead of using an indicator.

6.10 Add 5.0 ml APDC solution and mix. The pH should then be approximately 2.8.

6.11 Add 10.0 ml MIBK and shake vigorously for 3 minutes.

6.12 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.13 Aspirate the ketone layer, record the instrument reading for each sample and standard against the blank. Repeat, and average the duplicate results.

7. Calculations

7.1 Determine the ug/1 Cr in each sample from a plot of the instrument readings of standards. A working curve must be prepared with each set of samples. Report Cr concentrations as follows: Less than 10 ug/1, nearest ug/1; 10 ug/1 and above, two significant figures.

8. Precision and Accuracy

8.1 Precision and accuracy data are not available at this time.

9. Reference

9.1 Atomic Absorption Newsletter 6, p. 128 (1967).

CHROMIUM, HEXAVALENT

Method 218.4 (Atomic Absorption, chelation-extraction)

STORET NO. 01032

1. Scope and Application
    1.1 This method covers the determination of dissolved hexavalent chromium in drinking, surface and saline waters. The method may also be applicable to certain domestic and industrial wastes after filtration provided that no interferring substances are present. (See 4.1.)
    1.2 The method may be used to analyze samples containing from 10 to 250 *u*g of chromium per liter.
2. Summary of the Method
    2.1 This method is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the atomic absorption spectrophotometer.
    2.2 Hexavalent chromium may also be chelated with pyrrolidine dithiocarbamic acid in chloroform as described in section 9.2 of the atomic absorption text found in this manual. A pH of 2.3 must be maintained throughout the extraction.
    2.3 The diphenylcarbazide colorimetric procedure as found on p. 192 of "Standard Methods for the Examination of Water and Wastewater", 14th edition, 1975, may also be used.
3. Sample Handling and Preservation
    3.1 Stability of hexavalent chromium is not completely understood at this time. Therefore, the chelation and extraction should be carried out as soon as possible.
    3.2 To retard the chemical activity of hexavalent chromium, the sample should be transported and stored until time of anlysis at 4°C.
4. Interferences
    4.1 High concentrations of other reactive metals, as may be found in wastewaters, may interfere. The method is free from interferences from elements normally occurring in fresh water.
5. Instrumental Parameters (General)
    5.1 Chromium hollow cathode lamp.
    5.2 Wavelength: 357.9 nm
    5.3 Fuel: Acetylene
    5.4 Oxidant: Air
    5.5 Type of Flame: Fuel rich (adjust for organic solvent)
6. Reagents
    6.1 Ammonium pyrrolidine dithiocarbamate (APDC) solution. Dissolve 1.0 g APDC in demineralized water and dilute to 100 ml. Prepare fresh daily.

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6.2 Bromophenol blue indicator solution: Dissolve 0.1 g bromophenol blue in 100 ml 50-percent ethanol.

6.3 Chromium standard solution I, 1.0 ml = 100 *ug* Cr: Dissolve 0.2829 g pure, dried $K_2Cr_2O_7$ in demineralized water and dilute to 1000 ml.

6.4 Chromium standard solution II, 1.0 ml = 10.0 *ug* Cr: Dilute 100 ml chromium standard solution I to 1000 ml with demineralized water.

6.5 Chromium standard solution III, 1.0 ml = 0.10 *ug* Cr: Dilute 10.0 ml chromium standard solution II to 1000 ml with demineralized water.

6.6 Methyl isobutyl ketone (MIBK).

6.7 Sodium hydroxide solution, 1 M: Dissolve 40 g NaOH in demineralized water and dilute to 1 liter.

6.8 Sulfuric acid, 0.12 M: Slowly add 6.5 ml concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 liter.

7. Procedure

7.1 Pipet a volume of sample containing less than 25 *ug* chromium (100 ml maximum) into a 200 ml volumetric flask, and adjust the volume to approximately 100 ml.

7.2 Prepare a blank and sufficient standards, and adjust the volume of each to approximately 100 ml.

7.3 Add 2 drops bromophenol blue indicator solution. (The pH adjustment to 2.4 may also be made with a pH meter instead of using an indicator.)

7.4 Adjust the pH by addition of 1 M NaOH solution dropwise until a blue color persists. Add 0.12 M H_2SO_4 dropwise until the blue color just disappears in both the standards and sample. Then add 2.0 ml of 0.12 M H_2SO_4 in excess. The pH at this point should be 2.4.

7.5 Add 5.0 ml APDC solution and mix. The pH should then be approximately 2.8.

7.6 Add 10.0 ml MIBK and shake vigorously for 3 minutes.

7.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

7.8 Aspirate the ketone layer and record the scale reading for each sample and standard against the blank. Repeat, and average the duplicate results.

8. Calculations

8.1 Determine the *ug*/l Cr^{+6} in each sample from a plot of scale readings of standards. A working curve must be prepared with each set of samples. Report Cr^{+6} concentrations as follows: Less than 10 *ug*/l, nearest *ug*/l; 10 *ug*/l and above, two significant figures.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using the (PDCA) extraction procedure and Cincinnati Ohio tap water spiked at a concentration of 50 *ug* Cr^{+6}/l the standard deviation was ±2.6 with a mean recovery of 96%.

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Environmental Protection
Agency

Environmental Monitoring and
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Research and Development

EPA

Test Method

Chromium, Dissolved Hexavalent (Atomic Absorption, Furnace Technique)—Method 218.5

1. Scope and Application

1.1 This method covers the determination of dissolved hexavalent chromium (Cr^{6+}) in drinking and surface waters. The method may also be applicable to certain domestic and industrial wastes after filtration provided that potential interferring substances are taken into account. (See 4.1.)

1.2 The method may be used to analyze samples containing from 5 to 100 μg of Cr^{6+} per liter. The range of the method may be extended upward by dilution.

2. Summary of Method

2.1 The method is based on the separation of Cr^{6+} from the sample by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernate is drawn off and the Cr^{6} precipitate resolubilized in nitric acid as trivalent chromium (Cr^{3+}) and quantified by furnace atomic absorption.

2.2 Hexavalent chromium may also be analyzed by the chelation/extraction technique (see Method 218.4 or the procedure described in 9.2 of the Atomic Absorption methods found in this manual).

3. Sample Handling and Preservation

3.1 For sample handling, cleaning glassware and the filtration procedure see part 4.1 of the Atomic Absorption Method section of this manual.

3.2 The sample must not be preserved by acidification, but instead transported and stored until time of analysis at 4°C.

3.3 Stability of Cr^{6+} in environmental samples is not completely understood at this time. The chemical nature of the sample matrix can have a definite affect on the chemistry of chromium. Therefore, the analysis should be carried out as soon as possible but no longer than 24 hours after collection.

4. Interferences

4.1 The possible interference from other elements which form stable chromates is not known at this time.

4.2 Samples with either sulfate or chloride concentrations above 1000 mg/liter should be diluted before analysis.

4.3 The potential reduction of Cr^{6+} from highly reductive substances increases as pH is lowered. When sulfites and sulfides are present the sample aliquot taken for analysis should be neutralized and aerated before beginning.

5. Instrument Parameters (General)

5.1 Drying Time and Temp: 30 sec-125°C.

5.2 Ashing Time and Temp: 30 sec-1000°C.

5.3 Atomizing Time and Temp: 10 sec-2700°C.

5.4 Purge Gas Atmosphere: Argon

5.5 Wavelength: 357.9nm

5.6 Other operating parameters should be as specified by the particular instrument manufacturer.

6. Special Apparatus

6.1 Glassware

6.1.1 Filtering flask, heavy wall, 1 liter capacity

6.1.2 Centrifuge tubes, heavy duty, conical, graduated, glass stoppered, 10 mL capacity

6.1.3 Pasteur pipets, borosilicate glass, 5 ¾ inches.

6.2 Centrifuge: any centrifuge capable of reaching 2000 rpm and accepting the centrifuge tubes described in 6.1.2 may be used.

6.3 pH Meter: a wide variety of instruments are commercially available and suitable for this work.

6.4 Test Tube Mixer: any mixer capable of thorough vortex is acceptable.

7. Reagents

7.1 Lead Nitrate Solution: Dissolve 33.1 grams of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL.

7.2 Ammonium Sulfate Solution: Dissolve 2.7 grams of ammonium sulfate, $(NH_4)_2SO_4$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL.

7.3 Calcium Nitrate Solution: Dissolve 11.8 grams of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL. 1 mL = 20 mg Ca.

7.4 Nitric Acid, conc.: Distilled reagent grade or equivalent to spectrograde quality.

7.5 Acetic Acid, Glacial: ACS reagent grade.

7.5.1 Acetic Acid, 10% (v/v): Dilute 10 mL glacial acetic acid to 100 mL with deionized distilled water.

7.6 Ammonium Hydroxide, 10% (v/v): Dilute 10 mL conc ammonium hydroxide, NH_4OH (analytical reagent grade), to 100 mL with deionized distilled water.

7.7 Hydrogen Peroxide, 30%: ACS reagent grade.

7.8 Potassium Dichromate Standard Solution: Dissolve 2.8285 grams of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in deionized distilled water and dilute to 1 liter. 1 mL = 1 mg Cr (1000 mg/L)

7.9 Trivalent Chromium Working Stock Solution: To 50 mL of the potassium dichromate standard solution (7.8) add 1 mL of 30% H_2O_2 (7.7) and 1 mL conc. HNO_3 (7.4) and dilute to 100 mL with deionized distilled water 1 mL = 0.5 mg Cr^{3+} Prepare fresh monthly or as needed.

8. Calibration

8.1 At the time of analysis prepare a blank and a series of at least four calibration standards from the Cr^{3+} working stock (7.9) that will adequately bracket the sample. The normal working range covers a concentration range of 5 to 100 ug Cr/L. Add to the blank and each standard 1 mL 30% H_2O_2 (7.7), 5 mL CONC HNO_3 (7.4), and 1 mL calcium nitrate solution (7.3) for each 100 mL of prepared solution before diluting to final volume. These calibration standard should be prepared fresh weekly or as needed.

8.2 The listed instrumental conditions (5.) and the stated calibration concentration range are for a Perkin-Elmer HGA-2100 based on the use of a 20µL injection, continous flow purge gas and non-pyrolytic graphite. The use of simultaneous background correction is required for both calibration and sample analysis.

9. Procedure

9.1 Transfer a 50 mL portion of the filtered sample to a 100mL Griffin beaker and adjust to pH 3.5±0.3 by adding 10% acetic acid dropwise. Record the volume of acid added and adjust the final result to account for the dilution.

Note: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to < 3, 10% NH_4OH (7.6) should be used to raise the pH to above 3.

9.2 Pipet a 10 mL aliquot of the adjusted sample into a centrifuge tube (6.1.2). Add 100µL of the lead nitrate solution (7.1), stopper the tube, mix the sample and allow to stand for 3 min

9.3 After the formation of lead chromate, retain the Cr^{3+} complex in solution by addition of 0.5 mL glacial acetic acid (7.5). Stopper and mix.

9.4 To provide adequate lead sulfate for coprecipitation add 100 mL ammonium sulfate solution (7.2), stopper and mix.

9.5 Place the stoppered centrifuge tube in the centrifuge, making sure that the tube is properly counterbalanced. Start the centrifuge and slowly increase the speed to 2000 rpm in small increments over a period of 5 min. Centrifuge the sample at 2000 rpm for 10 min.

Note 2: The speed of the centrifuge must be increased slowly to insure complete coprecipitation.

9.6 After centrifuging remove the tube and draw off the supernate using the apparatus detailed in Figure 1. As the pasteur pipet is lowered into the tube the supernate is sucked into the filtering flask. With care the supernate can be withdrawn to within approximately 0.1 mL above the precipitate.

9.7 To the remaining precipitate add 0.5 mL conc HNO_3 (7.4), 100µL 30% H_2O_2 (7.7) and 100µL calcium nitrate solution (7.3). Stopper the tube and mix using a vortex mixer to disrupt the precipitate and solubilize the lead chromate. Dilute to 10mL, mix and analyze in the same manner as the calibration standard (8.2).

9.8 For the general furnace procedure and calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

10. Verification

10.1 For every sample matrix analyzed verification is necessary to determine that neither a reducing condition nor a chemical interference affecting precipitation is present. This must be accomplished by analyzing a second 10mL aliquot of the pH adjusted filtrate (9.1) spiked with Cr^{6+} (7.8). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be of less than 30μg Cr^{6+}/L. To verify the absence of an interference the spike recovery should be between 85% and 115%.

10.2 If the addition of the spike extends the concentration beyond the range of the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

10.3 If the verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

11. Analytical Notes

11.1 Nitrogen should not be used as a purge gas because of possible CN band interference.

11.2 The use of pyrolytic graphite should be avoided when possible. Generally, pyrolytic graphite resulted in a more limited analytical working range and in some situations an enhancement effect.

11.3 Pipet tips have been reported to be a possible source of contamination. (See part 5.2.9 of the Atomic Absorption Methods section of this manual.)

11.4 The method of standard addition should not be required in as much as the Cr^{6+} has been separated from the original sample solution and redissolved in a uniform matrix having an absorption response coincident to the calibration curve.

11.5 Data to be entered into STORET (No. 01032) must be reported as μg/L.

12. Precision and Accuracy

12.1 In a single laboratory (EMSL) using a mixed industrial-domestic waste effluent containing 22 μg Cr^{6+}/L and spiked with a concentration of 50 μg Cr^{6+}/L the standard deviations were ± 1.0 and ± 2.7, respectively with a spike recovery of 94%.

12.2 Recoveries of a 40 μg Cr^{6+}/L spike in diluted tannery and plating waste effluents were 96% and 93%, respectively.

12.3 Using Cincinnati, Ohio tap water spiked at concentrations of 5,10, and 50 μg Cr^{6+}/L the standard deviations were ± 0.7, ±0.6, and ±0.6, respectively. Spike recovery at all three levels was 102%.

12.4 A 1000 μg Cr^{3+}/L standard solution analyzed by this method yielded a result of 8 μg Cr^{6+}/L with a relative standard deviation of 19%.

12.5 The data from 5 μg Cr^{6+}/L tap water spike was used to calculate method detection limit (MDL) with 99% confidence as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, *Environmental Science and Technology*, Vol. 15, Number 12, page 1426, December 1981. The calculated MDL for Cincinnati drinking water is 2.3 μg/L.

COBALT
Method 219.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01037
Dissolved 01035
Suspended 01036

Optimum Concentration Range: 0.5–5 mg/1 using a wavelength of 240.7 nm
Sensitivity: 0.2 mg/1
Detection Limit: 0.05 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.307 g of cobaltous chloride, $CoCl_2 \cdot 6H_2O$ (analytical reagent grade), in deionized distilled water. Add 10 ml of concentrated nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Co (1000 mg/1).
2. Prepare dilutions of the stock cobalt solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Cobalt hollow cathode lamp
2. Wavelength: 240.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of Flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. For levels of cobalt below 100 ug/1, either the Special Extraction Procedure, given in part 9.2 of the Atomic Absorption Methods section or the furnace technique, Method 219.2 is recommended.
2. Data to be entered into **STORET** must be reported as ug/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.20, 1.0 and 5.0mg Co/1, the standard deviations were ±0.013, ±0.01 and ±0.05, respectively. Recoveries at these levels were 98%, 98%, and 97%, respectively.

COBALT

Method 219.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01037
Dissolved 01035
Suspended 01036

Optimum Concentration Range: 5–100 ug/1
Detection Limit: 1 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–900°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 240.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic

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graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas but with reported lower sensitivity.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *ug/1*.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

COPPER
Method 220.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01042
Dissolved 01040
Suspended 01041

Optimum Concentration Range: 0.2–5 mg/1 using a wavelength of 324.7 nm
Sensitivity: 0.1 mg/1
Detection Limit: 0.02 mg/1

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of electrolyte copper (analytical reagent grade). Dissolve in 5 ml redistilled HNO_3 and make up to 1 liter with deionized distilled water. Final concentration is 1 mg Cu per ml (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Copper hollow cathode lamp
2. Wavelength: 324.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. For levels of copper below 50 *ug*/1, either the Special Extraction Procedure, given in part 9.2 of the Atomic Absorption Methods section or the furnace technique, Method 220.2, is recommended.
2. Numerous absorption lines are available for the determination of copper. By selecting a suitable absorption wavelength, copper samples may be analyzed over a very wide range of concentration. The following lines may be used:
   327.4 nm Relative Sensitivity 2
   216.5 nm Relative Sensitivity 7
   222.5 nm Relative Sensitivity 20
3. Data to be entered into **STORET** must be reported as *ug*/1.
4. The 2,9-dimethyl-1, 10-phenanthroline colorimetric method may also be used (Standard Methods, 14th Edition, p. 196).

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for copper were as follows:

Number of Labs	True Values ug/liter	Mean Value ug/liter	Standard Deviation ug/liter	Accuracy as % Bias
91	302	305	56	0.9
92	332	324	56	-2.4
86	60	64	23	7.0
84	75	76	22	1.3
66	7.5	9.7	6.1	29.7
66	12.0	13.9	9.7	15.5

COPPER

Method 220.2 (Atomic Absorption, furnace technique)

STORET NO. 01042
Dissolved 01040
Suspended 01041

Optimum Concentration Range: 5–100 ug/l
Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–900°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 324.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic

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graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. Background correction may be required if the sample contains high dissolved solids.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

GOLD

Method 231.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 71910

Optimum Concentration Range: 0.5–20 mg/1 using a wavelength of 242.8 nm
Sensitivity: 0.25 mg/1
Detection Limit: 0.1 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.1000 g of gold metal in a minimum volume of aqua regia†. Take to near dryness, cool, add 5 ml HCl, and dilute to 100 ml with deionized water. Store in an amber glass bottle. (1 ml = 1 mg Au).
2. A standard AAS solution of chloroauric acid, $HAuCl_4$, 1000 mg/1 in aqueous matrix is available from Alfa Products, Beverly, Massachusetts 01915. Cat. #88068.
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. distilled HNO_3. Place the beaker on a steam bath and evaporate to near dryness. Cool the beaker and cautiously add a 5 ml portion of aqua regia. (See below for preparation of aqua regia.†) Cover the beaker with a watch glass and return to the steam bath. Continue heating the covered beaker for 30 minutes. Remove cover and evaporate to near dryness. Cool and add 1:1 distilled HNO_3 (1 ml per 100 m1 dilution). Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentration. The sample is now ready for analysis.

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†Aqua regia-prepare immediately before use by carefully adding three volumes of conc. HCL to one volume of conc. HNO_3.

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Instrumental Parameters (General)

1. Gold hollow cathode lamp
2. Wavelength: 242.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. For concentrations of gold below 100 ug/1, the furnace procedure, Method 231.2, is recommended.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

GOLD

Method 231.2 (Atomic Absorption, furnace technique)

STORET NO. 71910

Optimum Concentration Range:	5–100 *u*g/1
Detection Limit:	1 *u*g/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–600°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 242.8 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of his manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite.

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2. The use of background correction is recommended.
3. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
4. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
5. Data to entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

IRIDIUM

Method 235.1 (Atomic Absorption, direct aspiration)

STORET NO. Total*

Optimum Concentration Range: 20–500 mg/1 using a wavelength of 264.0 nm
Sensitivity: 8 mg/1
Detection Limit: 3 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.147 g of ammonium chloroiridate $(NH_4)_2IrCl_6$, in a minimum volume of 1% (v/v) HCl and dilute to 100 ml with 1% HCl (1 ml = 5 mg Ir).
2. A standard AAS solution of chloroiridic acid, H_2IrCl_6, 1000 mg/1 in aqueous matrix is available from Alfa Products, Beverly, Massachusetts 01915.
   Cat. #88072.
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. distilled HNO_3. Place the beaker on a steam bath and evaporate to near dryness. Cool the beaker and cautiously add a 5 ml portion of aqua regia. (See below for preparation of aqua regia.†) Cover the beaker with a watch glass and return to the steam bath. Continue heating the covered beaker for 30 minutes. Remove cover and evaporate to near dryness. Cool and add 1:1 distilled HNO_3 (1 ml per 100 ml dilution). Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentration. The sample is now ready for analysis.

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†Aqua regia-prepare immediately before use by carefully adding three volumes conc. HC1 to one volume of conc. HNO_3.

*Not Assigned

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Instrumental Parameters (General)

1. Iridium hollow cathode lamp
2. Wavelength: 264.0 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Reducing

Analysis Procedure

1. For analysis and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. For concentrations of iridium below 3 mg/1, the furnace procedure, Method 235.2, is recommended.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

IRIDIUM

Method 235.2 (Atomic Absorption, furnace technique)

STORET NO. Total*

Optimum Concentration Range: 0.1–1.5 mg/l
Detection Limit: 0.03 mg/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calculation standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–600°C.
3. Atomizing Time and Temp: 10 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 264.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

*Not Assigned

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. The 208.9 nm line is a factor of 3X more sensitive than the 264.0 nm line, but requires a very narrow slit to be discriminated from nearby non-absorbing lines.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

IRON

Method 236.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01045
Dissolved 01046
Suspended 01044

Optimum Concentration Range: 0.3–5 mg/1 using a wavelength of 248.3 nm
Sensitivity: 0.12 mg/1
Detection Limit: 0.03 mg/1

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 g of pure iron wire (analytical reagent grade) and dissolve in 5 ml redistilled HNO_3, warming if necessary. When solution is complete make up to 1 liter with deionized distilled water. 1 ml = 1 mg Fe (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Iron hollow cathode lamp
2. Wavelength: 248.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. The following lines may also be used:
   248.8 nm Relative Sensitivity 2
   271.9 nm Relative Sensitivity 4
   302.1 nm Relative Sensitivity 5
   252.7 nm Relative Sensitivity 6
   372.0 nm Relative Sensitivity 10
2. Data to be reported into **STORET** must be reported as ug/1.
3. The 1,10-phenanthroline colorimetric method may also be used (Standard Methods, 14th Edition, p. 208).
4. For concentrations of iron below 0.05 mg/1, either the Special Extraction Procedure given in part 9.2 of the Atomic Absorption Methods section or the furnace procedure, Method 236.2, is recommended.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for iron were as follows:

Number Of Labs	True Values ug/liter	Mean Value ug/liter	Standard Deviation ug/liter	Accuracy as % Bias
82	840	855	173	1.8
85	700	680	178	−2.8
78	350	348	131	−0.5
79	438	435	183	−0.7
57	24	58	69	141
54	10	48	69	382

IRON

Method 236.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01045
Dissolved 01046
Suspended 01044

Optimum Concentration Range: 5–100 *ug*/1
Detection Limit: 1 *ug*/1

Preparation of Standard Solution

1. Stock Solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1000°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 248.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 *ul* injection, continuous flow purge gas and non-pyrolytic

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graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *ug/1*.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

LEAD

Method 239.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01051
Dissolved 01049
Suspended 01050

Optimum Concentration Range: 1–20 mg/1 using a wavelength of 283.3 nm
Sensitivity: 0.5 mg/1
Detection Limit: 0.1 mg/1

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete acidify with 10 ml redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Pb (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Lead hollow cathode lamp
2. Wavelength: 283.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. The analysis of this metal is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust the burner to maximize the absorbance reading with a lead standard. Then, aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal.
2. For levels of lead below 200 *ug*/1, either the Special Extraction Procedure given in part 9.2 of the Atomic Absorption Methods section or the furnace technique, Method 239.2, is recommended.
3. The following lines may also be used:
   217.0 nm Relative Sensitivity 0.4
   261.4 nm Relative Sensitivity 10
4. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
5. Data to be entered into **STORET** must be reported as *ug*/1.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for lead were as follows:

Number of Labs	True Values *ug*/liter	Mean Value *ug*/liter	Standard Deviation *ug*/liter	Accuracy as % Bias
74	367	377	128	2.9
74	334	340	111	1.8
64	101	101	46	-0.2
64	84	85	40	1.1
61	37	41	25	9.6
60	25	31	22	25.7

LEAD

Method 239.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01051
Dissolved 01049
Suspended 01050

Optimum Concentration Range: 5–100 ug/1
Detection Limit: 1 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Lanthanum Nitrate Solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 ml conc. HNO_3 and dilute to 1000 ml with deionized distilled water. 1 ml = 50 mg La.
3. Working Lead Solution: Prepare dilutions of the stock lead solution to be used as calibration standards at the time of analysis. Each calibration standard should contain 0.5% (v/v) HNO_3. To each 100 ml of diluted standard add 10 ml of the lanthanum nitrate solution.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.
2. To each 100 ml of prepared sample solution add 10 ml of the lanthanum nitrate solution.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–500°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 283.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure in the calculation see "Furnace Procedure", part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Greater sensitivity can be achieved using the 217.0 nm line, but the optimum concentration range is reduced. The use of a lead electrodeless discharge lamp at this lower wavelength has been found to be advantageous. Also a lower atomization temperature (2400°C) may be preferred.
4. To suppress sulfate interference (up to 1500 ppm) lanthanum is added as the nitrate to both samples and calibration standards. (Atomic Absorption Newsletter Vol. 15, No. 3, p 71, May-June 1976.)
5. Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.
6. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
7. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
8. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
9. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 25, 50, and 100 ug Pb/1, the standard deviations were ±1.3, ±1.6, and ±3.7, respectively. Recoveries at these levels were 88%, 92%, and 95% respectively.

MAGNESIUM

Method 242.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 00927
Dissolved 00925
Suspended 00926

Optimum Concentration Range: 0.02–0.5 mg/1 using a wavelength of 285.2 nm
Sensitivity: 0.007 mg/1
Detection Limit: 0.001 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.829 g of magnesium oxide, MgO (analytical reagent grade), in 10 ml of redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 0.50 mg Mg (500 mg/1).
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions in 250 ml conc. HCl, (Caution: Reaction is violent), and dilute to 500 ml with deionized distilled water.
3. Prepare dilutions of the stock magnesium solution to be used as calibration standards at the time of analysis. To each 10 ml volume of calibration standard and sample alike add 1.0 ml of the lanthanum chloride solution, i.e., 20 ml of standard or sample + 2 ml $LaCl_3$ = 22 ml.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. For the analysis of total magnesium in domestic and industrial effluents, the procedures for the determination of total metals as given in parts 4.1.3 and 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.
2. For ambient waters, a representative aliquot of a well-mixed sample may be used directly for analysis. If suspended solids are present in sufficient amounts to clog the nebulizer, the sample may be allowed to settle and the supernatant liquid analyzed directly.
3. Samples should be preserved with (1:1) nitric acid to a pH of 2 at the time of collection.

Instrumental Parameters (General)

1. Magnesium hollow cathode lamp
2. Wavelength: 285.2 nm

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3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The interference caused by aluminum at concentrations greater than 2 mg/1 is masked by addition of lanthanum. Sodium, potassium and calcium cause no interference at concentrations less than 400 mg/1.
2. The following line may also be used:
   202.5 nm Relative Sensitivity 25
3. To cover the range of magnesium values normally observed in surface waters (0.1–20 mg/1), it is suggested that either the 202.5 nm line be used or the burner head be rotated. A 90° rotation of the burner head will produce approximately one-eighth the normal sensitivity.
4. Data to be entered into **STORET** must be reported as mg/1.
5. The gravimetric method may also be used (Standard Methods, 14th Edition, p 221).

Precision and Accuracy

1. In a single laboratory (EMSL), using distilled water spiked at concentrations of 2.1 and 8.2 mg Mg/1 the standard deviations were ±0.1 and ±0.2, respectively. Recoveries at both of these levels were 100%.

MANGANESE

Method 243.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01055
Dissolved 01056
Suspended 01054

Optimum Concentration Range: 0.1–3 mg/1 using a wavelength of 279.5 nm
Sensitivity: 0.05 mg/1
Detection Limit: 0.01 mg/1

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 g of manganese metal (analytical reagent grade) and dissolve in 10 ml of redistilled HNO_3. When solution is complete, dilute to 1 liter with 1% (V/V) HCl. 1 ml = 1 mg Mn (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Manganese hollow cathode lamp
2. Wavelength: 279.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. For levels of manganese below 25 *ug*/1, either the furnace procedure, Method 243.2, or the Special Extraction Procedure given in part 9.2 of the Atomic Absorption Methods section is recommended. The extraction is carried out at a pH of 4.5 to 5. The manganese chelate is very unstable and the analysis must be made without delay to prevent its resolution in the aqueous phase.
2. The following line may also be used:
   403.1 nm Relative Sensitivity 10.
3. Data to be entered into **STORET** must be reported as *ug*/1.
4. The persulfate colorimetric method may also be used (Standard Methods, 14th Edition, p 225).

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for manganese were as follows:

Number of Labs	True Values *ug*/liter	Mean Value *ug*/liter	Standard Deviation *ug*/liter	Accuracy as % Bias
77	426	432	70	1.5
78	469	474	97	1.2
71	84	86	26	2.1
70	106	104	31	-2.1
55	11	21	27	93
55	17	21	20	22

MANGANESE
Method 243.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01055
Dissolved 01056
Suspended 01054

Optimum Concentration Range: 1–30 *ug*/l
Detection Limit: 0.2 *ug*/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1000°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 279.5 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 *ul* injection, continuous flow purge gas and non-pyrolytic

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graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *ug/1*.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

MERCURY
Method 245.1 (Manual Cold Vapor Technique)

STORET NO. Total 71900
Dissolved 71890
Suspended 71895

1. Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potasssium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.

1.3 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 *ug* Hg/1 can be achieved; concentrations below this level should be reported as < 0.2 (see Appendix 11.2).

2. Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. If only dissolved mercury is to be determined, the sample should be filtered through an all glass apparatus before the acid is added. For total mercury the filtration is omitted.

4. Interference

4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/1 of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

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4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the **BOD** bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

4.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present (see Appendix 11.1).

5. Apparatus

5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

Note 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4–1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc.: Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content (See Note 3).

NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1 ml = 1 mg Hg.

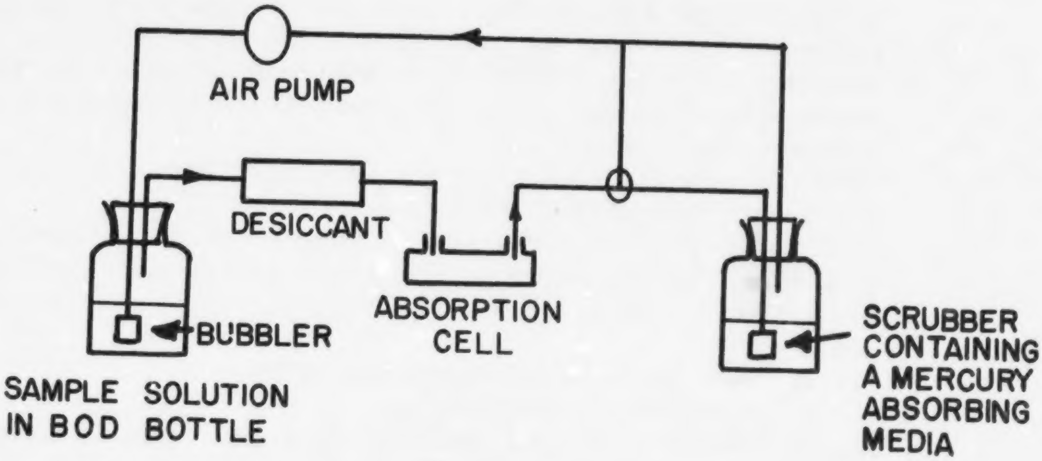
AIR PUMP
DESICCANT
BUBBLER
ABSORPTION CELL
SAMPLE SOLUTION IN BOD BOTTLE
SCRUBBER CONTAINING A MERCURY ABSORBING MEDIA

FIGURE 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10.0 ml aliquots of the working mercury solution containing 0 to 1.0 ug of mercury to a series of 300 ml **BOD** bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) to each bottle. Add 15 ml of $KMnO_4$ (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintined at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 ml of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (See Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the **BOD** bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4
b) 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580–13 or #580–22.

8. Procedure

8.1 Transfer 100 ml, or an aliquot diluted to 100 ml, containing not more than 1.0 ug of mercury, to a 300 ml **BOD** bottle. Add 5 ml of sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) mixing after each addition. Add 15 ml of potassium permanganate solution (6.5) to each sample bottle. For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. After a delay of at least 30 seconds add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

9. Calculation

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$ug\ Hg/l = \left(\begin{matrix} ug\ Hg\ in \\ aliquot \end{matrix}\right) \left(\frac{1{,}000}{\text{volume of aliquot in ml}}\right)$$

9.3 Report mercury concentrations as follows: Below 0.2 ug/1, <0.2; between 1 and 10 ug/1, one decimal; above 10 ug/1, whole numbers.

10. Precision and Accuracy

10.1 In a single laboratory (EMSL), using an Ohio River composite sample with a background mercury concentration of 0.35 ug/1, spiked with concentrations of 1.0, 3.0 and 4.0 ug/1, the standard deviations were ±0.14, ±0.10 and ±0.08, respectively. Standard deviation at the 0.35 level was ±0.16. Percent recoveries at the three levels were 89, 87, and 87%, respectively.

10.2 In a joint **EPA/ASTM** interlaboratory study of the cold vapor technique for total mercury in water, increments of organic and inorganic mercury were added to natural waters. Recoveries were determined by difference. A statistical summary of this study follows:

Number of Labs	True Values ug/liter	Mean Value ug/liter	Standard Deviation ug/liter	Accuracy as % Bias
76	0.21	0.349	0.276	66
80	0.27	0.414	0.279	53
82	0.51	0.674	0.541	32
77	0.60	0.709	0.390	18
82	3.4	3.41	1.49	0.34
79	4.1	3.81	1.12	−7.1
79	8.8	8.77	3.69	−0.4
78	9.6	9.10	3.57	−5.2

11. Appendix

11.1 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EMSL has not encountered such samples. This is mentioned only to caution the analyst of the possibility. A simple correction that may be used is as follows: If an interference has been found to be present (4.4), the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

11.2 If additional sensitivity is required, a 200 ml sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 ug/1 the standard deviations were ±0.027, ±0.006, ±0.01 and ±0.004. Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.

11.3 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water", p 349, Method D3223 (1976).

Bibliography

1. Kopp, J. F., Longbottom, M. C. and Lobring, L. B., "Cold Vapor Method for Determining Mercury", AWWA, vol 64, p. 20, Jan., 1972.
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D3223–73, p 343 (1976).
3. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 156 (1975).

MERCURY

Method 245.2 (Automated Cold Vapor Technique)

STORET NO. Total 71900
Dissolved 71890
Suspended 71895

1. Scope and Application
   1.1 This method is applicable to surface waters. It may be applicable to saline waters, wastewaters, effluents, and domestic sewages providing potential interferences are not present (See Interference 4).
   1.2 The working range is 0.2 to 20.0 *ug* Hg/1.
2. Summary of Method
   2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.
   2.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, an automated persulfate oxidation step following the automated addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.
3. Sample Handling and Preservation
   3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection.(1) If only dissolved mercury is to be determined, the sample should be filtered before the acid is added. For total mercury the filtration is omitted.
4. Interference (See **NOTE 1**)
   4.1 Some sea waters and waste-waters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.
   4.2 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run under oxidizing conditions, without stannous sulfate, would determine if this type of interference is present.

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4.3 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.

4.4 Samples containing solids must be blended and then mixed while being sampled if total mercury vlaues are to be reported.

NOTE 1: All the above interferences can be overcome by use of the Manual Mercury method in this manual.

5. Apparatus

5.1 Technicon Auto Analyzer consisting of:

5.1.1 Sampler II with provision for sample mixing.

5.1.2 Manifold.

5.1.3 Proportioning Pump II or III.

5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116–0163) in series.

5.2 Vapor-liquid separator (Figure 1).

5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.

5.4 Atomic Absorption Spectrophotometer (See Note 2): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 2: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.7 Source of cooling water for jacketed mixing coil and connector A-7.

5.8 Heat lamp: A small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade

6.1.1 Sulfuric acid, 2 N: Dilute 56 ml of conc. sulfuric acid to 1 liter with distilled water.

6.1.2 Sulfuric acid, 10%: Dilute 100 ml conc. sulfuric acid to 1 liter with distilled water.

6.2 Nitric acid, Conc: Reagent grade of low mercury content.

6.2.1 Nitric Acid, 0.5% Wash Solution: Dilute 5 ml of conc. nitric acid to 1 liter with distilled water.

6.3 Stannous Sulfate: Add 50 g stannous sulfate to 500 ml of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.

NOTE 3: Stannous chloride may be used in place of stannous sulfate.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.

NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

6.5 Potassium Permanganate: 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of distilled water.

6.6 Potassium Permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.

6.7 Potassium Persulfate: 0.5% solution, w/v. Dissolve 5 g potassium persulfate in 1 liter of distilled water.

6.8 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg.

6.9 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.8) to obtain a working standard containing 0.1 *ug* per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 *ug* Hg/1.

6.10 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate (6.6) and 10% sulfuric acid (6.1.2).

7. Procedure

7.1 Set up manifold as shown in Figure 2.

7.2 Feeding all the reagents through the system with acid wash solution (6.2.1) through the sample line, adjust heating bath to 105°C.

7.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.

7.4 Arrange working mercury standards from 0.2 to 20.0 *ug* Hg/1 in sampler and start sampling. Complete loading of sample tray with unknown samples.

7.5 Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as:

a) equal volumes of 0.1 N $KMnO_4$ (6.6) and 10% H_2SO_4 (6.1.2).

b) 0.25% iodine in a 3% KI solution, is recommended.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and North Cassidy St., Columbus, Ohio 43219, Cat. #580–13 or #580–22.

7.6 After the analysis is complete put all lines except the H_2SO_4 line in distilled water to wash out system. After flushing, wash out the H_2SO_4 line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

8. Precision and Accuracy

8.1 In a single laboratory (SEWL), using distilled water standards at concentrations of 0.5, 1.0, 2.0, 5.0, 10.0 and 20.0 *u*g Hg/1, the standard deviations were ±0.04, ±0.07, ±0.09, ±0.20, ±0.40 and ±0.84 *u*g/1, respectively.

8.2 In a single laboratory (SEWL), using surface water samples spiked with ten organic mercurials at the 10 *u*g/1 level, recoveries ranged from 87 to 117%. Recoveries of the same ten organic mercurials in distilled water at the 10 *u*g/1 level, ranged from 92% to 125%.

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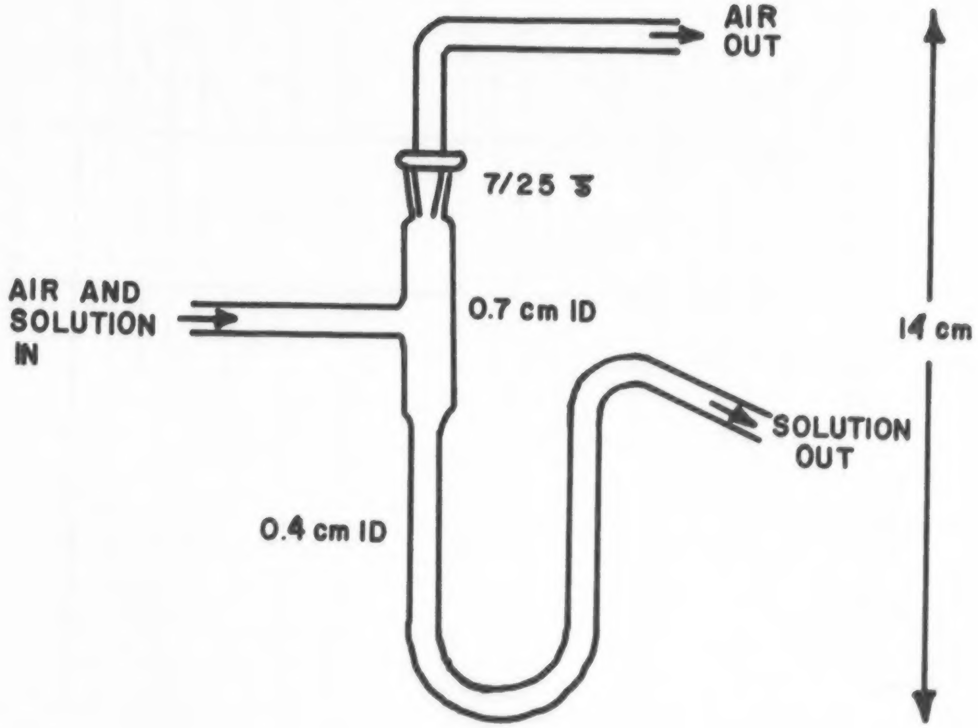
AIR
OUT
7/25 ₮
AIR AND
SOLUTION
IN
0.7 cm ID
14 cm
SOLUTION
OUT
0.4 cm ID

FIGURE 1. VAPOR LIQUID SEPARATOR

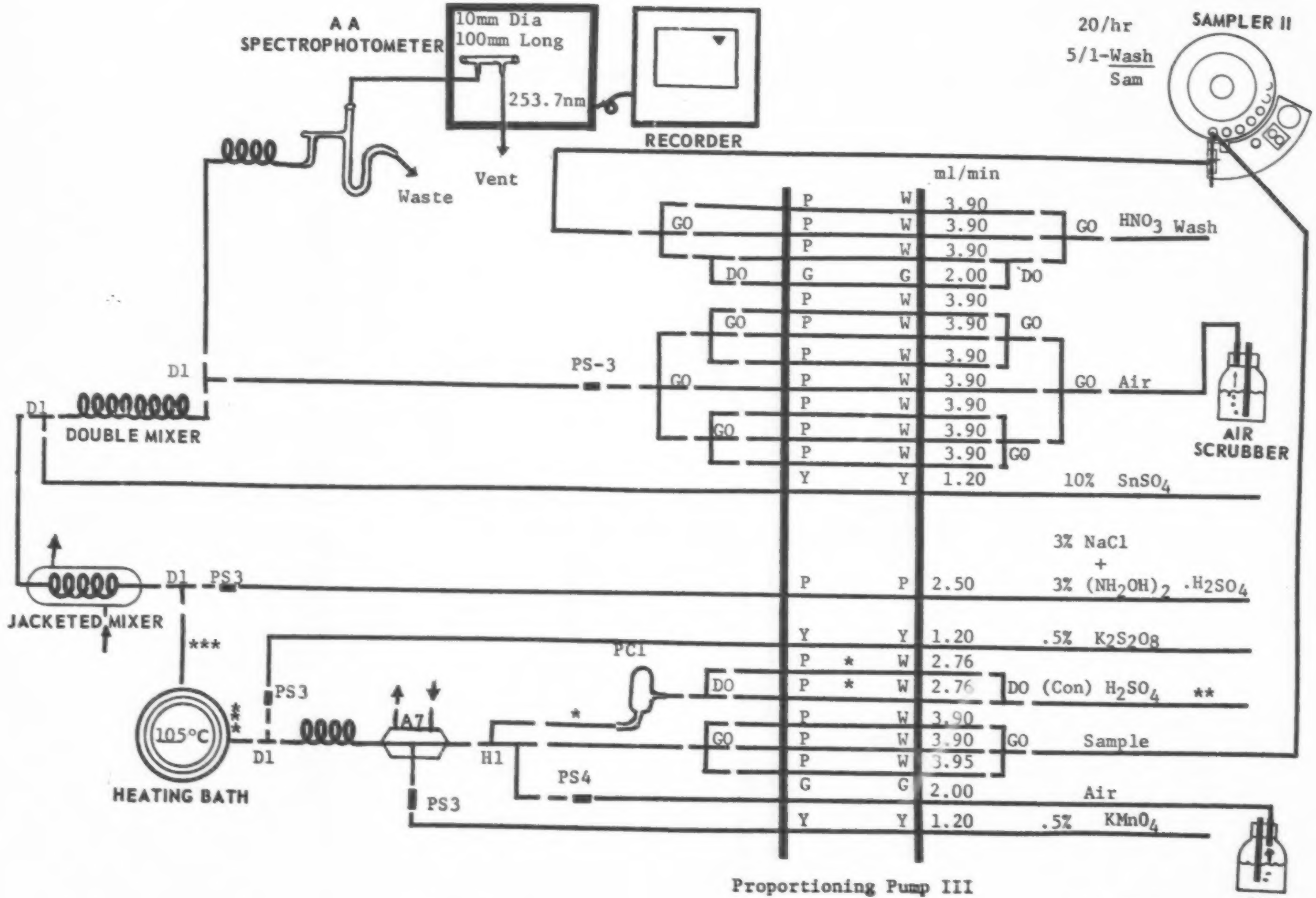
A A SPECTROPHOTOMETER
10mm Dia
100mm Long
253.7nm
Vent
Waste
RECORDER
SAMPLER II
20/hr
5/1-Wash/Sam
ml/min
HNO3 Wash
Air
AIR SCRUBBER
10% SnSO4
3% NaCl + 3% (NH2OH)2 ·H2SO4
.5% K2S2O8
(Con) H2SO4 **
Sample
Air
.5% KMnO4
AIR SCRUBBER
P W 3.90
P W 3.90
P W 3.90
G G 2.00
P W 3.90
P W 3.90
P W 3.90
P W 3.90
P W 3.90
P W 3.90
P W 3.90
Y Y 1.20
P P 2.50
Y Y 1.20
P * W 2.76
P * W 2.76
P W 3.90
P W 3.90
P W 3.95
G G 2.00
Y Y 1.20
GO
DO
PS-3
D1
DOUBLE MIXER
JACKETED MIXER
PS3
***
HEATING BATH
105°C
A7
H1
PS4
PC1
Proportioning Pump III
* Acid Flex
** Teflon
*** Glass

FIGURE 2 MERCURY MANIFOLD AA-I

MERCURY IN SEDIMENT

Method 245.5 (Manual Cold Vapor Technique)

1. Scope and Application
   - 1.1 This procedure(1) measures total mercury (organic † inorganic) in soils, sediments, bottom deposits and sludge type materials.
   - 1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.
2. Summary of Method
   - 2.1 A weighed portion of the sample is digested in aqua regia for 2 minutes at 95°C, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional cold vapor technique.
   - 2.2 An alternate digestion(2) involving the use of an autoclave is described in (8.2).
3. Sample Handling and Preservation
   - 3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.
   - 3.2 While the sample may be analyzed without drying, it has been found to be more convenient to analyze a dry sample. Moisture may be driven off in a drying oven at a temperature of 60°C. No mercury losses have been observed by using this drying step. The dry sample should be pulverized and thoroughly mixed before the aliquot is weighed.
4. Interferences
   - 4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.
   - 4.2 Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the **BOD** bottle should be purged before the addition of stannous sulfate.
5. Apparatus
   - 5.1 Atomic Absorption Spectrophotometer (See Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

     NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

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5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4–1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

NOTE 2: Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (See Note 3). The apparatus is assembled as shown in the accompanying diagram.

NOTE 3: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO_3.

6.2 Sulfuric Acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1 liter.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml.

NOTE 4: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg.

6.7 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.6) to obtain a working standard containing 0.1 ug/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10 ml aliquots of the working mercury solution (6.7) containing 0 to 1.0 ug of mercury to a series of 300 ml **BOD** bottles. Add enough distilled water to each bottle to make a total volume of 10 ml. Add 5 ml of aqua regia (6.1) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 ml distilled water and 15 ml of $KMnO_4$ solution (6.5) to each bottle and return to the water bath for 30 minutes. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass value and continue the aeration until the absorbance returns to its minimum value (See Note 5). Close the bypass value, remove the fritted tubing from the **BOD** bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4

b) 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave., and North Cassidy St., Columbus, Ohio 43219, Cat. #580–13 or #580–22.

8. Procedure

8.1 Weigh triplicate 0.2 g portions of dry sample and place in bottom of a **BOD** bottle. Add 5 ml of distilled water and 5 ml of aqua regia (6.1). Heat 2 minutes in a water bath at 95°C. Cool, add 50 ml distilled water and 15 ml potassium permanganate solution (6.5) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1).

8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 are added to the 0.2 g of sample. 5 ml of saturated $KMnO_4$ solution is added and the bottle covered with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 ml with distilled water and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the dead air space and continue as described under (7.1).

9. Calculation

9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$ug\ \text{Hg/g} = \frac{ug\ \text{Hg in the aliquot}}{\text{wt of the aliquot in gms}}$$

9.3 Report mercury concentrations as follows: Below 0.1 *ug*/gm, <0.1; between 0.1 and 1 *ug*/gm, to the nearest 0.01 *ug*; between 1 and 10 *ug*/gm, to nearest 0.1 *ug*; above 10 *ug*/gm, to nearest *ug*.

10. Precision and Accuracy

10.1 The following standard deviations on replicate sediment samples were recorded at the indicated levels; 0.29 *ug*/g ±0.02 and 0.82 *ug*/g ±0.03. Recovery of mercury at these levels, added as methyl mercuric chloride, was 97% and 94%, respectively.

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MOLYBDENUM

Method 246.1 (Atomic Absorption, direct aspiration)

STORET No. Total 01062
Dissolved 01060
Suspended 01061

Optimum Concentration Range: 1–40 mg/1 using a wavelength of 313.3 nm
Sensitivity: 0.4 mg/1
Detection Limit: 0.1 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.840 g of ammonium molybdate $(NH_4)_6Mo_7O_{24}\bullet4H_2O$ (analytical reagent grade) in deionized distilled water and dilute to 1 liter. 1 ml = 1 mg Mo (1000 mg/1).
2. Aluminum nitrate solution: Dissolve 139 g aluminum nitrate, $Al(NO_3)_3\bullet9H_2O$, in 150 ml of deionized distilled water; heat to effect solution. Allow to cool and make up to 200 ml.
3. Prepare dilutions of the stock molybdenum solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing. To each 100 ml of standard and sample alike, add 2 ml of the aluminum nitrate solution.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Molybdenum hollow cathode lamp
2. Wavelength: 313.3 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous Oxide
5. Type of flame: Fuel rich

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Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Interferences

1. With the recommended nitrous oxide-acetylene flame, interferences of calcium and other ions may be controlled by adding 1000 mg/1 of a refractory metal such as aluminum [Anal. Chem. Acta 44, 437 (1969)]. This should be done to both samples and standards alike.

Notes

1. Data to be entered into STORET must be reported as ug/1.
2. For concentrations of molybdenum below 0.2 mg/1, the furnace procedure, Method 246.2, is recommended.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.30, 1.5 and 7.5 mg Mo/1, the standard deviations were ±0.007, ±0.02 and ±0.07, respectively. Recoveries at these levels were 100%, 96% and 95%, respectively.

MOLYBDENUM

Method 246.2 (Atomic Absorption, furnace technique)

STORET No. Total 01062
Dissolved 01060
Suspended 01061

Optimum Concentration Range: 3–60 ug/1
Detection Limit: 1 *ug*/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1400°C.
3. Atomizing Time and Temp: 15 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 313.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure", part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite.
2. Background correction may be required if the sample contains high dissolved solids.
3. The use of nitrogen as a purge gas is not recommended.
4. For every sample matrix analyzed, verfication is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

NICKEL

Method 249.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01067
Dissolved 01065
Suspended 01066

Optimum Concentration Range: 0.3–5 mg/1 using a wavelength of 232.0 nm
Sensitivity: 0.15 mg/1
Detection Limit: 0.04 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.953 g of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ (analytical reagent grade) in deionized distilled water. Add 10 ml of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Ni (1000 mg/1).
2. Prepare dilutions of the stock nickel solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Nickel hollow cathode lamp
2. Wavelength: 232.0 nm
3, Fuel: Acetylene
4. Oxidant: Air
5. Type of Flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Interferences

1. The 352.4 nm wavelength is less susceptible to spectral interference and may be used. The calibration curve is more linear at this wavelength; however, there is some loss of sensitivity.

Notes

1. For levels of nickel below 100 *u*g/1, either the Special Extraction Procedure, given in part 9.2 of the Atomic Absorption Methods section or the furnace technique, Method 249.2, is recommended.
2. Data to be entered into **STORET** must be reported as *u*g/1.
3. The heptoxime method may also be used (Standard Methods, 14th Edition, p 232).

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.20, 1.0 and 5.0 mg Ni/1, the standard deviations were ±0.011, ±0.02 and ±0.04, respectively. Recoveries at these levels were 100%, 97% and 93%, respectively.

NICKEL

Method 249.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01067
Dissolved 01065
Suspended 01066

Optimum Concentration Range: 5-50 ug/l
Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec-800°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 232.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic

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graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

OSMIUM
Method 252.1 (Atomic Absorption, direct aspiration)

STORET NO. Total*

Optimum Concentration Range: 2–100 mg/1 using a wavelength of 290.9 nm
Sensitivity: 1 mg/1
Detection Limit: 0.3 mg/1

Preparation of Standard Solution

1. Stock Solution: A standard AAS solution of osmium tetroxide, OsO_4, 1000 mg/1 in aqueous matrix is available from Alfa Products, Beverly, Massachusetts 01915. Cat. #88084
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared to contain 1% (v/v) HNO_3 and 1% (v/v) H_2SO_4.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer a representative 100 ml aliquot of the well mixed sample to a Griffin beaker and add 1 ml of conc. distilled HNO_3. Place the beaker on a steam bath or hot plate and warm for 15 minutes. Cool the beaker and filter to remove insoluble material that could clog the atomizer. Add 1 ml of conc. H_2SO_4 and adjust the volume back to 100 ml. The sample is now ready for analysis.

Instrumental Parameters (General)

1. Osmium hollow cathode lamp
2. Wavelength: 290.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Analysis Procedure

1. For the analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

*Not Assigned

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Notes

1. Osmium tetroxide, the usual commercial form, is very volatile and highly toxic. Care should be exercised when working with this compound.
2. For concentrations of osmium below 0.5 mg/1 the furnace procedure, Method 252.2, is recommended.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

OSMIUM

Method 252.2 (Atomic Absorption, furnace technique)

STORET NO. Total*

Optimum Concentration Range: 50–500 *ug*/1
Dectection Limit: 20 *ug*/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 1% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method", except omit the addition of H_2SO_4 on the final volume adjustment. Sample solutions for analysis should contain 1% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–105°C.
2. Ashing Time and Temp: See NOTE 3 below.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 290.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. Osmium tetroxide, the usual commercial form, is very volatile and highly toxic. Care should be exercised when working with this compound.

*Not Assigned

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2. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 *u*l injection, continuous flow purge gas and non-pyrolytic graphite.
3. Since O_sO_4 volatilizes near 150°C, the allowable ashing temperature must be verified in the sample matrix being analyzed.
4. The use of background correction is recommended.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

PALLADIUM

Method 253.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01210

Optimum Concentration Range: 0.5–15 mg/1 using a wavelength of 247.6 nm
Sensitivity: 0.25 mg/1
Detection Limit: 0.1 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.1000 g of palladium wire in a minimum volume of aqua regia and evaporate just to dryness. Add 5 ml conc. HCl and 25 ml deionized water and warm until dissolution is complete. Dilute to 100 ml with deionized water. (1 ml = 1 mg Pd).
2. A standard AAS solution of palladous chloride, $PdCl_2$, 1000 mg/1 in aqueous matrix is available from Alfa Products, Beverly, Massachusetts 01915. Cat. #88085.
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. distilled HNO_3. Place the beaker on a steam bath and evaporate to near dryness. Cool the beaker and cautiously add a 5 ml portion of aqua regia. (See below for preparation of aqua regia.†) Cover the beaker with a watch glass and return to the steam bath. Continue heating the covered beaker for 30 minutes. Remove cover and evaporate to near dryness. Cool and add 1:1 redistilled HNO_3 (1 ml per 100 ml dilution). Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentration. The sample is now ready for analysis.

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†Aqua regia-prepare immediately before use by carefully adding three volume of conc. HCl to one volume of conc. HNO_3.

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Instrumental Parameters (General)

1. Palladium hollow cathode lamp
2. Wavelength: 247.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. For concentrations of palladium below 0.25 mg/1, the furnace procedure, Method 253.2, is recommended.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

PALLADIUM

Method 253.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01210

Optimum Concentration Range: 20–400 ug/1
Detection Limit: 5 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solution for analysis should contain 0.5%(v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1000°C.
3. Atomizing Time and Temp: 10 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 247.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

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2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

PLATINUM

Method 255.1 (Atomic Absorption, direct aspiration)

STORET NO. Total*

Optimum Concentration Range: 5–75 mg/1 using a wavelength of 265.9 nm
Sensitivity: 2 mg/1
Detection Limit: 0.2 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.1000 g of platinum metal in a minimum volume of aqua regia and evaporate just to dryness. Add 5 ml HCl and 0.1 g NaCl and again evaporate just to dryness. Dissolve the residue in 20 ml of (1:1) HCl and dilute to 100 ml with deionized water. (1 ml = 1 mg Pt).
2. A standard AAS solution of chloroplatinic acid, H_2PtCl_6, 1000 mg/1 in aqueous matrix is available from Alfa Products, Beverly, Massachusetts 01915.
   Cat. #88086.
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared to contain 0.5%(v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. distilled HNO_3. Place the beaker on a steam bath and evaporate to near dryness. Cool the beaker and cautiously add a 5 ml portion of aqua regia. (See below for preparation of aqua regia.†). Cover the beaker with a watch glass and return to the steam bath. Continue heating the covered beaker for 30 minutes. Remove cover and evaporate to near dryness. Cool and add 1:1 distilled HNO_3 (1 ml per 100 ml dilution). Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentration. The sample is now ready for analysis.

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†Aqua regia-prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO_3.

*Not Assigned

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Instrumental Parameters (General)

1. Platinum hollow cathode lamp
2. Wavelength: 265.9 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. For concentrations of platinum below 1.0 mg/1, the furnace procedure, Method 255.2, is recommended.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

PLATINUM
Method 255.2 (Atomic Absorption, furnace technique)

STORET NO. Total*

Optimum Concentration Range: 0.1–2 mg/1
Detection Limit: 0.02 mg/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v)HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1300°C.
3. Atomizing Time and Temp: 10 sec–2800°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 265.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can

*Not Assigned

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be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

POTASSIUM

Method 258.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 00937
Dissolved 00935
Suspended 00936

Optimum Concentration Range: 0.1–2 mg/1 using a wavelength of 766.5 nm
Sensitivity: 0.04 mg/1
Detection Limit: 0.01 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.1907 g of KCl (analytical reagent grade), dried at 110°C, in deionized distilled water and make up to 1 liter. 1 ml = 0.10 mg K (100 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. For the analysis of total potassium in domestic and industrial effluents, the procedures for the determination of total metals as given in parts 4.1.3 and 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.
2. For ambient waters, a representative aliquot of a well mixed sample may also be used directly for analysis. If suspended solids are present in sufficient amounts to clog the nebulizer, the sample may be allowed to settle and the supernatant liquid analyzed directly.

Instrumental Parameters (General)

1. Potassium hollow cathode lamp
2. Wavelength: 766.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Slightly oxidizing

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Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. In air–acetylene or other high temperature flames (> 2800°C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1000 *ug*/ml) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks should be analyzed to correct for potassium impurities in the buffer stock.
2. The 404.4 nm line may also be used. This line has a relative sensitivity of 500.
3. To cover the range of potassium values normally observed in surface waters (0.1–20 mg/1), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides approximately one-eighth the normal sensitivity.
4. The flame photometric or colorimetric methods may also be used (Standard Methods, 14th Edition, p 234 & 235).
5. Data to be entered into **STORET** must be reported as mg/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using distilled water samples spiked at concentrations of 1.6 and 6.3 mg K/1. The standard deviations were ±0.2 and ±0.5, respectively. Recoveries at these levels were 103% and 102%, respectively.

RHENIUM
Method 264.1 (Atomic Absorption, direct aspiration)

STORET NO. Total*

Optimum Concentration Range: 50–1000 mg/1 using a wavelength of 346.0 nm
Sensitivity: 15 mg/1
Detection Limit: 5 mg/1

Preparation of Standard Solution

1. Stock solution: Dissolve 1.554 g of potassium perrhenate, $KReO_4$, in 200 ml deionized water. Dilute to 1 liter with 1% (v/v) H_2SO_4. (1 ml = 1 mg Re).
2. A standard AAS solution of ammonium perrhenate, NH_4ReO_4, 1000 mg/1 in aqueous matrix is available from Alfa Products, Beverly, Massachussetts 01915. Cat. #88089.
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using 1% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer a representative 100 ml aliquot of the well mixed sample to a Griffin beaker and add 1 ml of conc. distilled HNO_3. Place the beaker on a steam bath or hot plate and warm for 15 minutes. Cool and filter to remove insoluble material that could clog the atomizer. Adjust the volume back to 100 ml. The sample is now ready for analysis.

Instrumental Parameters (General)

1. Rhenium hollow cathode lamp
2. Wavelength: 346.0 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous Oxide
5. Type of flame: Fuel rich

Analysis Procedure

1. For the analysis procedure and the calculation, see "direct aspiration" part 9.1 of the Atomic Absorption Methods section of this manual.

*Not Assigned

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Notes

1. For concentrations of rhenium below 10 mg/1, the furnace procedure, Method 264.2, is recommended.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

RHENIUM

Method 264.2 (Atomic Absorption, furnace technique)

STORET NO. Total*

Optimum Concentration Range: 0.5–5 mg/1

Detection Limit: 0.2 mg/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards should be diluted to contain 1% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 1%(v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–300°C.
3. Atomizing Time and Temp: 10 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 346.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

*Not Assigned

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite.
2. Background correction may be required if the sample contains high dissolved solids.
3. Since many rhenium compounds volatilize near 300°C, the allowable ashing temperature should be verified in the sample matrix being analyzed.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

RHODIUM

Method 265.1 (Atomic Absorption, direct aspiration)

STORET NO. Total*

Optimum Concentration Range: 1–30 mg/1 using a wavelength of 343.5 nm
Sensitivity: 0.3 mg/1
Detection Limit: 0.05 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.3768 g of ammonium chlororhodite, $(NH_4)_3RhCl_6 \cdot H_2O$, in a minimum volume of 10% (v/v) HCl and dilute to 100 ml with 10% HCl. (1 ml = 1mg Rh).
2. A standard AAS solution of rhodium trichloride, $RhCl_3$, 1000 mg/1 in aqueous matrix is available from Alfa Products, Beverly, Massachusetts 01915.
   Cat. #88090
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. distilled HNO_3. Place the beaker on a steam bath and evaporate to near dryness. Cool the beaker and cautiously add a 5 ml portion of aqua regia. (See below for preparation of aqua regia.†) Cover the beaker with a watch glass and return to the steam bath. Continue heating the covered beaker for 30 minutes. Remove cover and evaporate to near dryness. Cool and add 1:1 distilled HNO_3 (1 ml per 100 ml dilution). Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentration. The sample is now ready for analysis.

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†Aqua regia-prepare immediately before use by carefully adding three volumes of conc. HC1 to one volume of conc. HNO_3.

*Not Assigned

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Instrumental Parameters (General)

1. Rhodium hollow cathode lamp
2. Wavelength: 343.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. For concentrations of rhodium below 0.2 mg/1, the furnace procedure, Method 265.2, is recommended.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

RHODIUM
Method 265.2 (Atomic Absorption, furnace technique)

STORET NO. Total*

Optimum Concentration Range: 20–400 ug/1
Detection Limit: 5 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1200°C.
3. Atomizing Time and Temp: 10 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 343.5 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

*Not Assigned

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite.
2. Background correction may be required if the sample contains high dissolved solids.
3. The use of nitrogen as a purge gas is not recommended.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

RUTHENIUM

Method 267.1 (Atomic Absorption, direct aspiration)

STORET NO. Total*

Optimum Concentration Range: 1–50 mg/l using a wavelength of 349.9 nm
Sensitivity: 0.5 mg/l
Detection Limit: 0.2 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.2052 g of ruthenium chloride, $RuCl_3$, in a minimum volume of 20% (v/v) HCl and dilute to 100 ml with 20% HCl. (1 ml = 1 mg Ru).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using 1% (v/v) HCl.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer a representative 100 ml aliquot of the well mixed sample to a Griffin beaker and add 2 ml of distilled (1:1) HCl. Place the beaker on a steam bath or hot plate and warm at 95°C for 15 minutes. Cool the beaker and filter the sample to remove insoluble material that could clog the atomizer. Adjust the volume back to 100 ml. The sample is now ready for analysis.

Instrumental Parameters (General)

1. Ruthenium hollow cathode lamp
2. Wavelength: 349.9 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

*Not Assigned

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Notes

1. For concentrations of ruthenium below 0.5 mg/1, the furnace procedure, Method 267.2, is recommended.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

RUTHENIUM

Method 267.2 (Atomic Absorption, furnace technique)

STORET NO. Total*

Optimum Concentration Range: 0.1–2 mg/1
Detection Limit: 0.02 mg/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. Using distilled (1:1) HCl, the calibration standards should be diluted to contain 1% (v/v) HCl.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 1% (v/v) HCl.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–400°C.
3. Atomizing Time and Temp: 10 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 349.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

*Not Assigned

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite.
2. Background correction may be required if the sample contains high dissolved solids.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

SELENIUM

Method 270.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01147
Dissolved 01145
Suspended 01146

Optimum Concentration Range: 5–100 *ug*/1
Detection Limit: 2 *ug*/1

Preparation of Standard Solution

1. Stock Selenium Solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 ml. 1 ml = 1 mg Se (1000 mg/1).
2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 ml.
3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.
4. Working Selenium Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2 ml of 30% H_2O_2 and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.
2. Cool and bring back to 50 ml with deionized distilled water.
3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace. NOTE: If solubilization or digestion is not required adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30% H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

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Instrument Parameters

1. Drying time and temperature: 30 sec @ 125°C
2. Charring time and temperature: 30 sec @ 1200°C
3. Atomizing time and temperature: 10 sec @ 2700°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 196.0 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Selenium analysis suffers interference from chlorides (> 800 mg/1) and sulfate (> 200 mg/1). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/1, both samples and standards should be prepared to contain 1% nickel.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to entered into STORET must be reported as *u*g/1.

Precision and Accuracy

1. Using a sewage treatment plant effluent containing <2 *u*g/1 and spiked with a concentration of 20 *u*g/1, a recovery of 99% was obtained.
2. Using a series of industrial waste effluents spiked at a 50 *u*g/1 level, recoveries ranged from 94 to 112%.
3. Using a 0.1% nickel nitrate solution as a synthetic matrix with selenium concentrations of 5, 10, 20, 40, 50, and 100 *u*g/1, relative standard deviations of 14.2, 11.6, 9.3, 7.2, 6.4 and 4.1%, respectively, were obtained at the 95% confidence level.

4. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 5, 10, and 20 *u*g Se/1, the standard deviations were ±0.6, ±0.4, and ±0.5, respectively. Recoveries at these levels were 92%, 98%, and 100%, respectively.

Reference:

"Determining Selenium in Water, Wastewater, Sediment and Sludge By Flameless Atomic Absorption Spectroscopy", Martin, T. D., Kopp, J. F. and Ediger, R. D. Atomic Absorption Newsletter 14, 109 (1975).

SELENIUM

Method 270.3 (Atomic Absorption, gaseous hydride)

STORET NO. Total 01147
Dissolved 01145
Suspended 01146

1. Scope and Application
   - 1.1 The gaseous hydride method determines inorganic selenium when present in concentrations at or above 2 *u*g/1. The method is applicable to drinking water and most fresh and saline waters, in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel and silver.
2. Summary of Method
   - 2.1 Selenium in the sample is reduced from the +6 oxidation state to the +4 oxidation state by the addition of $SnCl_2$. Zinc is added to the acidified sample, producing hydrogen and converting the selenium to the hydride, SeH_2. The gaseous selenium hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the method is 2–20 *u*g/1 using the 196.0 nm wavelength.
3. Comments
   - 3.1 In analyzing drinking water and most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of selenium to establish adequate recovery.
   - 3.2 Organic forms of selenium must be converted to an inorganic form and organic matter must be oxidized before beginning the analysis. The oxidation procedure given in method 206.5 (Standard Methods, 14*th* Ed. 404B, p 285, Procedure 4.1) should be used.
   - 3.3 For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.
   - 3.4 For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
   - 3.5 Data to be entered into STORET must be reported as *u*g/1.
4. Precision and Accuracy
   - 4.1 Ten replicate solutions of selenium oxide at the 5, 10 and 15 *u*g/1 level were analyzed by a single laboratory. Standard deviations at these levels were ±0.6, ±1.1 and ±2.9 with recoveries of 100, 100 and 101%. (Caldwell, J. S., Lishka, R. J., and McFarren, E. F., "Evaluation of a Low-Cost Arsenic and Selenium Determination at Microgram per Liter Levels", JAWWA, vol 65, p. 731, Nov. 1973.)

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5. References

5.1 Except for the perchloric acid step, the procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 159, Method 301A(VII), (1975)

SILVER

Method 272.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01077
Dissolved 01075
Suspended 01076

Optimum Concentration Range: 0.1–4 mg/1 using a wavelength of 328.1 nm
Sensitivity: 0.06 mg/1
Detection Limit: 0.01 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in deionized distilled water, add 10 ml conc. HNO_3 and make up to 1 liter. 1 ml = 1 mg Ag (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using nitric acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.
3. Iodine Solution, 1 N: Dissolve 20 grams of potassium iodide, KI (analytical reagent grade) in 50 ml of deionized distilled water, add 12.7 grams of iodine, I_2 (analytical reagent grade) and dilute to 100 ml. Store in a brown bottle.
4. Cyanogen Iodide (CNI) Solution: To 50 ml of deionized distilled water add 4.0 ml conc. NH_4OH, 6.5 grams KCN, and 5.0 ml of 1.0 N I_2 solution. Mix and dilute to 100 ml with deionized distilled water. Fresh solution should be prepared every two weeks.(1)

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.3 of the Atomic Absorption Methods section of this manual have been found to be satisfactory; however, the residue must be taken up in dilute nitric acid rather than hydrochloric to prevent precipitation of AgCl.

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Instrumental Parameters (General)

1. Silver hollow cathode lamp
2. Wavelength: 328.1 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. For levels of silver below 30 *u*g/1, either the Special Extraction Procedure, given in part 9.2 of the Atomic Absorption Methods section or the furnace procedure, Method 272.2, is recommended.
2. Silver nitrate standards are light sensitive. Dilutions of the stock should be discarded after use as concentrations below 10 mg/1 are not stable over long periods of time.
3. If absorption to container walls or the formation of AgCl is suspected, make the sample basic using conc. NH_4OH and add 1 ml of (CNI) solution per 100 ml of sample. Mix the sample and allow to stand for 1 hour before proceeding with the analysis.(1)
4. The 338.2 nm wavelength may also be used. This has a relative sensitivity of 2.
5. Data to be entered into STORET must be reported as *u*g/1.

Precision and Accuracy

1. In a round-robin study reported by Standard Methods, a synthetic sample containing 50 *u*g Ag/1 was analyzed by 50 laboratories with a reported standard deviation of ±8.8 and a relative error 10.6%.

References

1. "The Use of Cyanogen Iodide (CNI) as a Stabilizing Agent for Silver in Photographic Processing Effluent Sample", Owerbach, Daniel, Photographic Technology Division, Eastman Kodak Company, Rochester, N.Y. 14650.
2. Standard Methods for Examination of Water and Wastewater, 14th Edition, p. 148, Method 301A.

SILVER

Method 272.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01077
Dissolved 01075
Suspended 01076

Optimum Concentration Range: 1–25 ug/l
Detection Limit: 0.2 ug/l

Preparation of Standard Solution

1. Stock Solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–400°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 328.1 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. Background correction may be required if the sample contains high dissolved solids.
3. The use of halide acids should be avoided.
4. If adsorption to container walls or formation of AgCl is suspected, see NOTE 3 under the Direct Aspiration Method 272.1.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
7. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
8. Data to be entered into STORET must be reported as *u*g/1.

Precision and Accuracy:

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 25, 50, and 75 *u*g Ag/1, the standard deviations were ±0.4, ±0.7, and ±0.9, respectively. Recoveries at these levels were 94%, 100% and 104%, respectively.

SODIUM

Method 273.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 00929
Dissolved 00930
Suspended 00928

Optimum Concentration Range: 0.03–1 mg/1 using a wavelength of 589.6 nm
Sensitivity: 0.015 mg/1
Detection Limit: 0.002 mg/1

Preparation of Standard Solutions

1. Stock Solution: Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in deionized distilled water and make up to 1 liter. 1 ml = 1 mg Na (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. For the analysis of total sodium in domestic and industrial effluents, the procedures for the determination of total metals as given in parts 4.1.3 and 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.
2. For ambient waters, a representative aliquot of a well-mixed sample may be used directly for analysis. If suspended solids are present in sufficient amounts to clog the nebulizer, the sample may be allowed to settle and the supernatant liquid analyzed directly.

Instrumental Parameters (General)

1. Sodium hollow cathode lamp
2. Wavelength: 589.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

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Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. The 330.2 nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.
2. Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1000 mg/1) to both standards and samples.
3. Data to be entered into STORET must be reported as mg/1.
4. The flame photometric method may also be used (Standard Methods, 14th Edition, p. 250).

Precision and Accuracy

1. In a single laboratory (EMSL), using distilled water samples spiked at levels of 8.2 and 52 mgNa/1, the standard deviations were ±0.1 and ±0.8, respectively. Recoveries at these levels were 102% and 100%.

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Environmental Protection
Agency

Environmental Monitoring and
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Research and Development

EPA

Test Method

Sodium (Atomic Absorption, furnace technique)—Method 273.2

Optimum Concentration Range: 1-30 µg/L
Detection Limit: 0.2 µg/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method."
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 250°C
3. Atomizing Time and Temp: 10 sec @ 2000°C.
4. Purge Gas atmosphere: Argon
5. Wavelength: 589.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" 9.3 of the Atomic Absorption method section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 µL injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. Samples containing concentrations higher than those given in the optimum range should be analyzed by either the direct aspiration method (Method 273.1) or the flame photometric method (Std. Methods, 14th Edition, p. 250).
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see 5.2.1 of the Atomic Absorption method section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in 8.5 of the Atomic Absorption methos section of this manual.

6. Data to be entered into STORET must be reported as μg/L.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

THALLIUM

Method 279.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01059
Dissolved 01057
Suspended 01058

Optimum Concentration Range: 1–20 mg/l using a wavelength of 276.8 nm
Sensitivity: 0.5 mg/l
Detection Limit: 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.303 g of thallium nitrate, $TlNO_3$ (analytical reagent grade) in deionized distilled water. Add 10 ml of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Tl (1000 mg/1).
2. Prepare dilutions of the stock thallium solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using nitric acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory if HCl is omitted.

Instrumental Parameters (General)

1. Thallium hollow cathode lamp
2. Wavelength: 276.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

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Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. For concentrations of thallium below 0.2 mg/1, the furnace procedure, Method 279.2, is recommended.
2. Data to be entered into **STORET** must be reported as *ug*/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.60, 3.0 and 15 mg Tl/1, the standard deviations were ±0.018, ±0.05 and ±0.2, respectively. Recoveries at these levels were 100%, 98% and 98%, respectively.

THALLIUM

Method 279.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01059
Dissolved 01057
Suspended 01058

Optimum Concentration Range: 5–100 ug/1
Detection Limit: 1 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 400°C
3. Atomizing Time and Temp: 10 sec @ 2400°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 276.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *u*g/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

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TIN

Method 282.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01102
Dissolved 01100
Suspended 01101

Optimum Concentration Range: 10–300 mg/1 using a wavelength of 286.3 nm
Sensitivity: 4 mg/1
Detection Limit: 0.8 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.000 g of tin metal (analytical reagent grade) in 100 ml of conc. HCl and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Sn (1000 mg/1).
2. Prepare dilutions of the stock tin solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Tin hollow cathode lamp
2. Wavelength: 286.3 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous Oxide
5. Type of flame: Fuel rich

Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. For concentrations of tin below 2 mg/1, the furnace procedure, Method 282.2, is recommended.
2. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent spiked at concentrations of 4.0, 20 and 60 mg Sn/1, the standard deviations were ±0.25, ±0.5 and ±0.5, respectively. Recoveries at these levels were 96%, 101%, and 101%, respectively.

TIN

Method 282.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01102
Dissolved 01100
Suspended 01101

Optimum Concentration Range: 20–300 *ug*/1
Detection Limit: 5 *ug*/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 2% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.3 of the Atomic Absorption Methods section of this manual should be followed including the addition of sufficient 1:1 HCl to dissolve the digested residue for the analysis of suspended or total tin. The sample solutions used for analysis should contain 2% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–600°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmospere: Argon.
5. Wavelength: 224.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. Tin analysis is sensitive to chloride concentration. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess of 5 mg of ammonium nitrate to the furnace and ash using a ramp necessary or with incremental steps until the recommended ashing temperature is reached. Extended ashing times have been reported to improve precision.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

TITANIUM

Method 283.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01152
Dissolved 01150
Suspended 01151

Optimum Concentration Range: 5–100 mg/1 using a wavelength of 365.3 nm
Sensitivity: 2 mg/1
Detection Limit: 0.4 mg/1

Preparation of Standard Solution

1. Stock solution: Dissolve 1.000 g of titanium metal (powder or small pieces) in 200 ml 6N HCl. Heat to near 100°C to effect dissolution. Cool and dilute to 1 liter with deionized distilled water. (1 ml = 1 mg Ti (1000 mg/l)
2. Potassium chloride solution: Dissolve 95 g potassium chloride, KCl, in distilled water and make up to 1 liter.
3. Prepare dilutions of the stock titanium solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing. To each 100 ml of standard and sample alike, add 2 ml of potassium chloride solution.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.3 of the Atomic Absorption Methods section of this manual have been found to be satisfactory with the following modification. For processing total and suspended titanium, concentrated H_2SO_4 (2 ml per 100 ml of final dilution) must be added in addition to the nitric acid. Reflux the sample adding additional nitric acid as needed. When solubilization is complete, heat until the appearance of SO_3 fumes. Cool and add sufficient distilled nitric acid so that the final dilution contains 0.5% (v/v) HNO_3.

Instrumental Parameters (General)

1. Titanium hollow cathode lamp
2. Wavelength: 365.3 nm
3. Fuel: Acetylene

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4. Oxidant: Nitrous Oxide
5. Type of flame: Fuel rich

Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration" part 9.1 of the Atomic Absorption Methods section of this manual.

Interferences

1. A number of elements increase the sensitivity of titanium. To control this problem, potassium (1000 mg/l) must be added to standards and samples alike. [Atomic Absorption Newsletter 6, p 86 (1967)]

Notes

1. For concentrations of titanium below 1.0 mg/1, the furnace procedure, Method 283.2, is recommended.
2. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent spiked at concentrations of 2.0, 10 and 50 mg Ti/1, the standard deviations were ±0.07, ±0.1 and ±0.4, respectively. Recoveries at these levels were 97%, 91% and 88%, respectively.

TITANIUM

Method 283.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01152
Dissolved 01150
Suspended 01151

Optimum Concentration Range: 50–500 ug/l
Detection Limit: 10 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis.
3. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1400°C.
3. Atomizing Time and Temp: 15 sec–2800°C.
4. Purge Gas Atmosphere: Argon.
5. Wavelength: 365.4 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite.
2. Background correction may be required if the sample contains high dissolved solids.
3. Because of possible chemical interactions, nitrogen should not be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

VANADIUM

Method 286.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01087
Dissolved 01085
Suspended 01086

Optimum Concentration Range: 2–100 mg/1 using a wavelength of 318.4 nm
Sensitivity: 0.8 mg/1
Detection Limit: 0.2 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7854 g of vanadium pentoxide, V_2O_5 (analytical reagent grade) in 10 ml of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg V (1000 mg/1).
2. Aluminum nitrate solution: Dissolve 139 g aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, in 150 ml of deionized distilled water; heat to effect solution. Allow to cool and make up to 200 ml.
3. Prepare dilutions of the stock vanadium solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing. To each 100 ml of standard and sample alike, add 2 ml of the aluminum nitrate solution.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Vanadium hollow cathode lamp
2. Wavelength: 318.4 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

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Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration" part 9.1 of the Atomic Absorption Methods section of this manual.

Interferences

1. It has been reported that high concentrations of aluminum and titanium increase the sensitivity of vanadium. This interference can be controlled by adding excess aluminum (1000 ppm) to both samples and standards. [Talanta 15, 871 (1968)].

Notes

1. For concentrations of vanadium below 0.5 mg/1, the furnace procedure, Method 286.2, is recommended.
2. The gallic acid colorimetric method may also be used (Standard Methods, 14th Edition, p 260).
3. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent spiked at concentrations of 2.0, 10 and 50 mg V/1, the standard deviations were ±0.10, ±0.1 and ±0.2, respectively. Recoveries at these levels were 100%, 95% and 97%, respectively.

VANADIUM

Method 286.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01087
Dissolved 01085
Suspended 01086

Optimum Concentration Range: 10–200 *ug*/1
Detection Limit: 4 *ug*/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solution for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1400°C.
3. Atomizing Time and Temp: 15 sec–2800°C.
4. Purge Gas Atmosphere: Argon.
5. Wavelength: 318.4 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. Background correction may be required if the sample contains high dissolved solids.
3. Because of possible chemical interaction, nitrogen should not be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

ZINC

Method 289.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01092
Dissolved 01090
Suspended 01091

Optimum Concentration Range: 0.05–1 mg/1 using a wavelength of 213.9 nm
Sensitivity: 0.02 mg/1
Detection Limit: 0.005 mg/1

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of zinc metal (analytical reagent grade) and dissolve cautiously in 10 ml HNO_3. When solution is complete make up to 1 liter with deionized distilled water. 1 ml = 1 mg Zn (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters

1. Zinc hollow cathode lamp
2. Wavelength: 213.9 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For the analysis procedure and the calculation, see "direct aspiration" part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. High levels of silicon may interfere.
2. The air-acetylene flame absorbs about 25% of the energy at the 213.9 nm line.
3. The sensitivity may be increased by the use of low-temperature flames.
4. Some sample container cap liners can be a source of zinc contamination. To circumvent or avoid this problem, the use of polypropylene caps is recommended.
5. The dithizone colorimetric method may also be used (Standard Methods, 14th Edition, p 265).
6. For concentrations of zinc below 0.01 mg/1, either the Special Extraction Procedure given in part 9.2 of the Atomic Absorption Methods section or the furnace procedure, Method 289.2, is recommended.
7. Data to entered into Storet must be reported as ug/1.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for zinc were as follows:

Number of Labs	True Values ug/liter	Mean Value ug/liter	Standard Deviation ug/liter	Accuracy as % Bias
86	281	284	97	1.2
89	310	308	114	-0.7
82	56	62	28	11.3
81	70	75	28	6.6
62	7	22	26	206
61	11	17	18	56.6

ZINC

Method 289.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01092
Dissolved 01090
Suspended 01091

Optimum Concentration Range: 0.2–4 ug/1
Detection Limit: 0.05 ug/1

Preparation of Standard Solution

1. Stock Solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solution for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–400°C.
3. Atomizing Time and Temp: 10 sec–2500°C.
4. Purge Gas Atmosphere: Argon.
5. Wavelength: 213.9 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. The analysis of zinc by the graphite furnace is extremely sensitive and very subject to contamination from the work area, reagents, and pipet tips. Since all these factors affect the precision and accuracy, zinc should be analyzed by the direct aspiration procedure whenever possible.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

ACIDITY

Method 305.1 (Titrimetric)

STORET NO. 70508

1. Scope and Application
   1.1 This method is applicable to surface waters, sewages and industrial wastes, particularly mine drainage and receiving streams, and other waters containing ferrous iron or other polyvalent cations in a reduced state.
   1.2 The method covers the range from approximately 10 mg/1 acidity to approximately 1000 mg/1 as $CaCO_3$, using a 50 ml sample.
2. Summary of Method
   2.1 The pH of the sample is determined and a measured amount of standard acid is added, as needed, to lower the pH to 4 or less. Hydrogen peroxide is added, the solution boiled for several minutes, cooled, and titrated electrometrically with standard alkali to pH 8.2.
3. Definitions
   3.1 This method measures the mineral acidity of a sample plus the acidity resulting from oxidation and hydrolysis of polyvalent cations, including salts of iron and aluminum.
4. Interferences
   4.1 Suspended matter present in the sample, or precipitates formed during the titration may cause a sluggish electrode response. This may be offset by allowing a 15–20 second pause between additions of titrant or by slow dropwise addition of titrant as the endpoint pH is approached.
5. Apparatus
   5.1 pH meter, suitable for electrometric titrations.
6. Reagents
   6.1 Hydrogen peroxide (H_2O_2, 30% solution).
   6.2 Standard sodium hydroxide, 0.02 N.
   6.3 Standard sulfuric acid, 0.02 N.
7. Procedure
   7.1 Pipet 50 ml of the sample into a 250 ml beaker.
   7.2 Measure the pH of the sample. If the pH is above 4.0, add standard sulfuric acid (6.3) in 5.0 ml increments to lower the pH to 4.0 or less. If the initial pH of the sample is less than 4.0, the incremental addition of sulfuric acid is not required.
   7.3 Add 5 drops of hydrogen peroxide (6.1).
   7.4 Heat the sample to boiling and continue boiling for 2 to 4 minutes. In some instances, the concentration of ferrous iron in a sample is such that an additional amount of hydrogen peroxide and a slightly longer boiling time may be required.

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7.5 Cool the sample to room temperature and titrate electrometrically with standard sodium hydroxide (6.2) to pH 8.2.

8. Calculations

8.1 Acidity, as mg/1 $CaCO_3$ = $\frac{[(A \times B) - (C \times D)] \times 50{,}000}{\text{ml of sample}}$

where:

A = vol. of standard sodium hydroxide used in titration
B = normality of standard sodium hydroxide
C = volume of standard sulfuric acid used to reduce pH to 4 or less
D = normality of standard sulfuric acid

8.2 If it is desired to report acidity in millequivalents per liter, the reported values as $CaCO_3$ are divided by 50, as follows:

$$\text{Acidity as meq/l} = \frac{\text{mg/1 CaCO}_3}{50}$$

9. Precision

9.1 On a round robin conducted by ASTM on 4 acid mine waters, including concentrations up to 2000 mg/1, the precision was found to be ±10 mg/1.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", p 116, D 1067, Method E(1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 277, Method 402(4d) (1975).

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

Acidity (Titrimetric)— Method 305.2

1. Scope and Application

1.1 This method is applicable to rain, surface and other waters of pH less than 8.3.

1.2 This method is a measure of the concentration of strong and weak acids that react with hydroxyl ions. This includes the dissolved gases that are present.

1.3 The range of this method depends on the volume of sample titrated and upon the precision that the increments of titrant can be measured. If only 10 mL of sample is available for analysis, it is necessary to use a 50 μL syringe for dispensing the titrant in order to achieve a precision of less than 10 μeq/L.

2. Summary of Method

2.1 Samples are titrated with 0.02 N carbonate free NaOH solution. The end point is determined with a pH meter. Results are reported as microequivalents (μeq) per liter.

3. Sampling Handling and Storage.

3.1 The sample container must be filled completely, sealed and stored at 4°C. Care must be taken to minimize exposure of the sample to the atmosphere. Open the sample container immediately before analysis.

3.2 Analysis should be performed as soon as possible after collection.

4. Comments

4.1 Samples with an initial pH between 4.3 and 8.3 are subject to error due to the loss or gain of dissolved gases during sampling, storage and analyses.

5. Apparatus

5.1 pH meter and electrode(s), see Method 150.1 or 150.2.

5.2 Micro buret or micro syrings.

5.3 Teflon or glass magnetic stirring bar.

5.4 Magnetic stirrer.

5.5 Beakers or flasks.

6. Reagents

6.1 Standard sodium hydroxide solution, 1 N: Dissolve 40g NaOH in 250 mL distilled water. Cool and dilute to 1 liter with CO_2 free distilled water. Store in a polyolefin bottle and fitted with a soda lime tube or tight cap to protect from atmospheric CO_2.

6.2 Standard sodium hydroxide titrant, 0.02 N: Dilute 20.0 mL of 1 N NaOH with CO_2-free distilled water to 1 liter. Store in rubber stoppered bottle. Protect from atmospheric CO_2 by using a soda lime tube. Standardize against an 0.02 N potassium acid phthalate solution prepared by dissolving 4.085 g of anhydrous $KHC_8H_4O_4$ in CO_2 free distilled water and diluted to 1:1.

7. Procedure

7.1 Pipet an appropriate aliquot of sample into beaker of flask containing a small teflon on glass stirring bar. Use extreme care to minimize the sample surface disturbance.

7.2 Immerse pH electrode(s) into sample and stir at a rate that does not cause sample surface disturbance.

7.3 Titrate with 0.02 N NaOH (6.2) to pH 8.3. Titration should be made as quickly as possible to prevent absorption of atmospheric CO_2. Record volume of titrant.

8. Calculation

8.1 **Acidity**, μeq/L $= \frac{ml_B}{mL_S} \times N_B \times 10^5$

μeq/L = microequivalents per liter

mL_B = mL of NaOH titrant

mL_S = mL of sample

N_B = normality of titrant

9. Precision and Accuracy

9.1 Precision and accuracy data are not available.

References

1. Seymour, M.D., Schubert, S.A., Clayton, J.W. and Fernando, Q., Variation in the Acid Content of Rain Water in the Course of a Single Precipitation, Water, Air and Soil Pollution 10(2): 147-161, Aug. 1978.
2. Peden, M.E. and Skowron, Ionic Stability of Precipitation Samples; Atmospheric Environment, Vol. 12, pp. 2343-2349. 1978.
3. USGS, Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases, p. 39, (1970).
4. Annual Book of ASTM Standards, part 31, "Water," p. 107, D1067, (1978).
5. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 273, Method 402 (1975).

ALKALINITY

Method 310.1 (Titrimetric, pH 4.5)

STORET NO. 00410

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 ml.
   1.3 Automated titrimetric analysis is equivalent.
2. Summary of Method
   2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.
3. Comments
   3.1 The sample should be refrigerated at 4°C and run as soon as practical. Do not open sample bottle before analysis.
   3.2 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.
   3.3 For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an electrometric endpoint of pH 3.9, using the procedure in:
   Annual Book of ASTM Standards, Part 31, "Water", p 115, D-1067, Method D, (1976).
   3.4 Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.
4. Apparatus
   4.1 pH meter or electrically operated titrator that uses a glass electrode and can be read to 0.05 pH units. Standardize and calibrate according to manufacturer's instructions. If automatic temperature compensation is not provided, make titration at 25 ±2° C.
   4.2 Use an appropriate sized vessel to keep the air space above the solution at a minimum. Use a rubber stopper fitted with holes for the glass electrode, reference electrode (or combination electrode) and buret.
   4.3 Magnetic stirrer, pipets, flasks and other standard laboratory equipment.
   4.4 Burets, Pyrex 50, 25 and 10 ml.
5. Reagents
   5.1 Sodium carbonate solution, approximately 0.05 N: Place 2.5 ±0.2 g (to nearest mg) Na_2CO_3 (dried at 250°C for 4 hours and cooled in desiccator) into a 1 liter volumetric flask and dilute to the mark.

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5.2 Standard acid (sulfuric or hydrochloric), 0.1 N: Dilute 3.0 ml conc H_2SO_4 or 8.3 ml conc HC1 to 1 liter with distilled water. Standardize versus 40.0 ml of 0.05 N Na_2CO_3 solution with about 60 ml distilled water by titrating potentiometrically to pH of about 5. Lift electrode and rinse into beaker. Boil solution gently for 3–5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using:

$$N = \frac{A \times B}{53.00 \times C}$$

where:
A = g Na_2CO_3 weighed into 1 liter
B = ml Na_2CO_3 solution
C = ml acid used to inflection point

5.3 Standard acid (sulfuric or hydrochloric), 0.02 N: Dilute 200.0 ml of 0.1000 N standard acid to 1 liter with distilled water. Standardize by potentiometric titration of 15.0 ml 0.05 N Na_2CO_3 solution as above.

6. Procedure

6.1 Sample size

6.1.1 Use a sufficiently large volume of titrant ($>$ 20 ml in a 50 ml buret) to obtain good precision while keeping volume low enough to permit sharp end point.

6.1.2 For $<$ 1000 mg $CaCO_3$/1 use 0.02 N titrant

6.1.3 For $>$ 1000 mg $CaCO_3$/1 use 0.1 N titrant

6.1.4 A preliminary titration is helpful.

6.2 Potentiometric titration

6.2.1 Place sample in flask by pipetting with pipet tip near bottom of flask

6.2.2 Measure pH of sample

6.2.3 Add standard acid (5.2 or 5.3), being careful to stir thoroughly but gently to allow needle to obtain equilibrium.

6.2.4 Titrate to pH 4.5. Record volume of titrant.

6.3 Potentiometric titration of low alkalinity

6.3.1 For alkalinity of $<$20 mg/1 titrate 100–200 ml as above (6.2) using a 10 ml microburet and 0.02 N acid solution (5.3).

6.3.2 Stop titration at pH in range of 4.3–4.7, record volume and exact pH. Very carefully add titrant to lower pH exactly 0.3 pH units and record volume.

7. Calculations

7.1 Potentiometric titration to pH 4.5

$$\text{Alkalinity, mg/1 } CaCO_3 = \frac{A \times N \times 50{,}000}{\text{ml of sample}}$$

where:
A = ml standard acid
N = normality standard acid

7.2 Potentiometric titration of low alkalinity:

$$\text{Total alkalinity, mg/l CaCO}_3 = \frac{(2B - C) \times N \times 50{,}000}{\text{ml of sample}}$$

where:
B = ml titrant to first recorded pH
C = total ml titrant to reach pH 0.3 units lower
N = normality of acid

8. Precision and Accuracy

8.1 Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate, with the following results:

Increment as Alkalinity mg/liter, $CaCO_3$	Precision as Standard Deviation mg/liter, $CaCO_3$	Accuracy as Bias, %	Bias, mg/l, $CaCO_3$
8	1.27	+10.61	+0.85
9	1.14	+22.29	+2.0
113	5.28	- 8.19	-9.3
119	5.36	- 7.42	-8.8

(FWPCA Method Study 1, Mineral and Physical Analyses)

8.2 In a single laboratory (EMSL) using surface water samples at an average concentration of 122 mg $CaCO_3$/1, the standard deviation was ±3.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 278, Method 403, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", p 113, D-1067, Method B, (1976).

ALKALINITY

Method 310.2 (Colorimetric, Automated, Methyl Orange)

STORET NO. 00410

1. Scope and Application
   1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The applicable range is 10 to 200 mg/1 as $CaCO_3$.
   1.2 This method is not an approved NPDES method as cited in the Federal Register December 1, 1976 for samples containing turbidity or color.
2. Summary of Method
   2.1 Methyl orange is used as the indicator in this method because its pH range is in the same range as the equivalence point for total alkalinity, and it has a distinct color change that can be easily measured. The methyl orange is dissolved in a weak buffer at a pH of 3.1, just below the equivalence point, so that any addition of alkalinity causes a loss of color directly proportional to the amount of alkalinity.
3. Sample Handling and Preservation
   3.1 Sample should be refrigerated at 4°C and run as soon as practical. Do not open sample bottle before analysis.
4. Interferences
   4.1 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. If sample is filtered, this method is not approved for NPDES monitoring. Sample color that absorbs in the photometric range used will also interfere.
5. Apparatus
   5.1 Technicon AutoAnalyzer consisting of:
      5.1.1 Sampler I.
      5.1.2 Manifold.
      5.1.3 Proportioning pump.
      5.1.4 Colorimeter equipped with 15 mm tubular flow cell and 550 nm filters.
      5.1.5 Recorder equipped with range expander.
6. Reagents
   6.1 Methyl Orange: Dissolve 0.125 g of methyl orange in 1 liter of distilled water.
   6.2 pH 3.1 Buffer: Dissolve 5.1047 g of potassium acid phthalate in distilled water and add 87.6 ml 0.1 N HCl and dilute to 1 liter. Stable for one week.
   6.3 Methyl Orange-Buffered Indicator: Add 1 liter of pH 3.1 buffer (6.2) to 200 ml methyl orange solution (6.1) and mix well. Stable for 24 hours.
   6.4 Stock Solution: Dissolve 1.060 g of anhydrous sodium carbonate (oven-dried at 250°C for 4 hours) in distilled water and dilute to 1000 ml. 1.0 ml = 1.00 mg $CaCO_3$.

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6.4.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/l as $CaCO_3$
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
18.0	180
20.0	200

7. Procedure

7.1 No advance sample preparation is required. Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings on sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

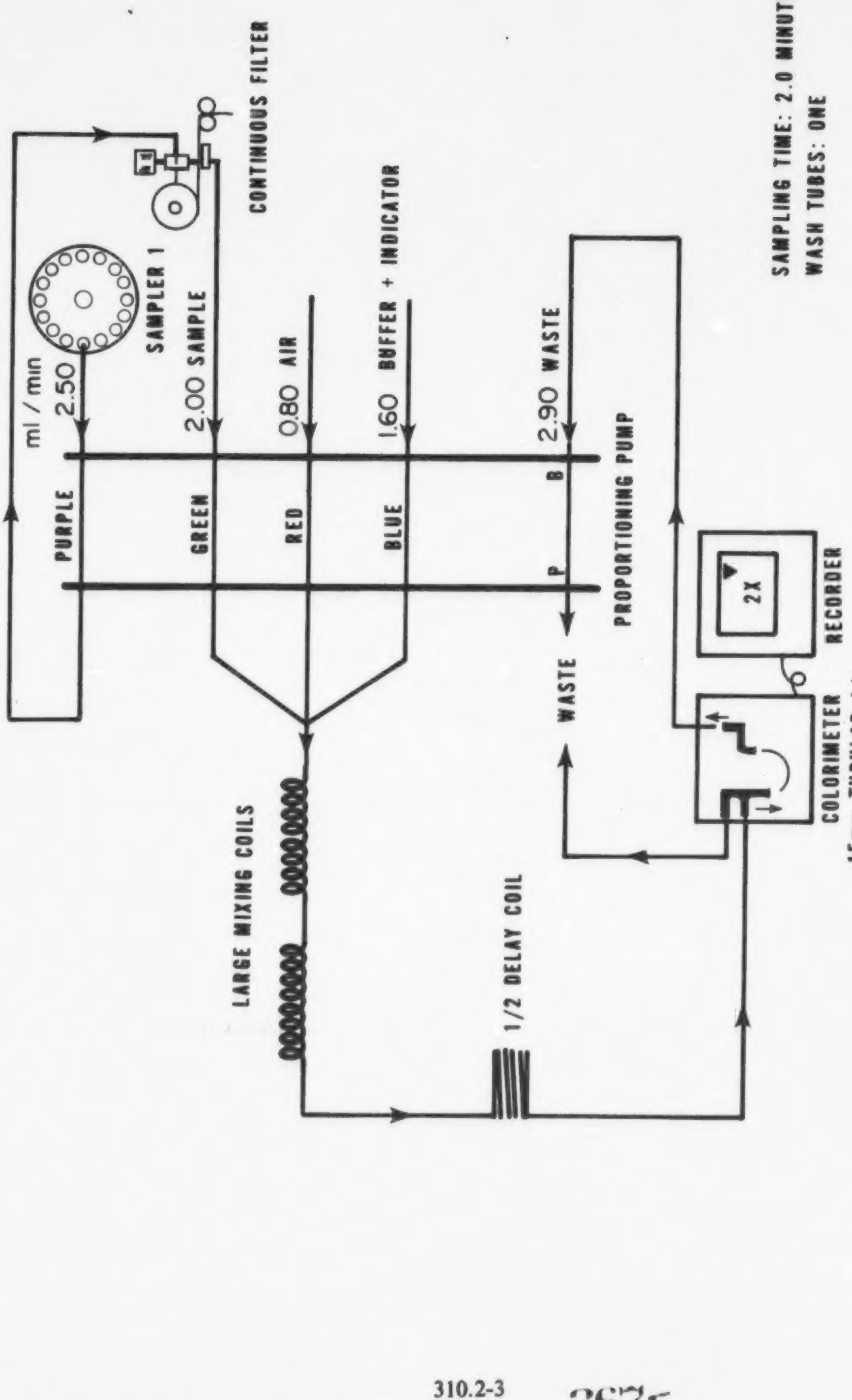
9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 15, 57, 154, and 193 mg/1 as $CaCO_3$ the standard deviation was ±0.5.

9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 31 and 149 mg/1 as $CaCO_3$ recoveries were 100% and 99%, respectively.

Bibliography

1. Technicon Auto Analyzer Methodology, Bulletin 1261, Technicon Controls, Inc., Chauncey, N.Y. (1961).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 278, Method 403 (1975).



ml / min
2.50
2.00 SAMPLE
0.80 AIR
1.60 BUFFER + INDICATOR
2.90 WASTE
SAMPLER 1
CONTINUOUS FILTER
PURPLE
GREEN
RED
BLUE
P
B
PROPORTIONING PUMP
WASTE
LARGE MIXING COILS
1/2 DELAY COIL
2X
RECORDER
COLORIMETER
15mm TUBULAR f/c
550 nm FILTERS

SAMPLING TIME: 2.0 MINUTES
WASH TUBES: ONE

FIGURE 1. ALKALINITY MANIFOLD AA-I

BROMIDE

Method 320.1 (Titrimetric)

STORET NO. 71870

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial waste effluents.
   1.2 The concentration range for this method is 2–20 mg bromide/1.
2. Summary of Method
   2.1 After pretreatment to remove interferences, the sample is divided into two aliquots. One aliquot is analyzed for iodide by converting the iodide to iodate with bromine water and titrating iodometrically with phenylarsine oxide (PAO) or sodium thiosulfate. The other aliquot is analyzed for iodide plus bromide by converting these halides to iodate and bromate with calcium hypochlorite and titrating iodometrically with PAO or sodium thiosulfate. Bromide is then calculated by difference.
3. Sample Handling and Preservation
   3.1 Store at 4°C and analyze as soon as possible.
4. Interferences
   4.1 Iron, manganese and organic matter can interfere; however, the calcium oxide pretreatment removes or reduces these to insignificant concentrations.
   4.2 Color interferes with the observation of indicator and bromine-water color changes. This interference is eliminated by the use of a pH meter instead of a pH indicator and the use of standardized amounts of oxidant and oxidant-quencher.
5. Reagents
   5.1 Acetic Acid Solution (1:8): Mix 100 ml of glacial acetic acid with 800 ml of distilled water.
   5.2 Bromine Water: In a fume hood, add 0.2 ml bromine to 500 ml distilled water. Stir with a magnetic stirrer and a Teflon-coated stirring bar for several hours or until the bromine dissolves. Store in a glass-stoppered, colored bottle.
   5.3 Calcium Carbonate ($CaCO_3$): Powdered.
   5.4 Calcium Hypochlorite Solution ($Ca(OCl)_2$): Add 35 g of $Ca(OCl)_2$ to approximately 800 ml of distilled water in a 1 liter volumetric flask. Stir on a magnetic stirrer for approximately 30 minutes. Dilute to 1 liter and filter. Store in a glass-stoppered, colored flask.
   5.5 Calcium Oxide (CaO): Anhydrous, powdered.
   5.6 Hydrochloric Acid Solution (1:4): Mix 100 ml of HCl (sp. gr. 1.19) with 400 ml of distilled water.

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5.7 Potassium Iodide (KI): Crystals, ACS Reagent Grade.

5.8 Sodium Acetate Solution (275 g/1): Dissolve 275 g sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in distilled water. Dilute to 1 liter and filter.

5.9 Sodium Chloride (NaCl): Crystals, ACS Reagent Grade.

5.10 Sodium Formate Solution (500 g/1): Dissolve 50 g sodium formate ($NaCHO_2$) in hot distilled water and dilute to 100 ml.

5.11 Sodium Molybdate Solution (10 g/1): Dissolve 1 g sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) in distilled water and dilute to 100 ml.

5.12 Sulfuric Acid Solution (1:4): Slowly add 200 ml H_2SO_4 (sp. gr. 1.84) to 800 ml of distilled water.

5.13 Phenylarsine Oxide (0.0375N): Hach Chemical Co., or equivalent. Standardize with 0.0375 N potassium biiodate (5.19, 5.23).

5.14 Phenylarsine Oxide Working Standard (0.0075 N): Transfer 100 ml of commercially available 0.0375 N phenylarsine oxide (5.13) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.15 Commercially available starch indicator such as thyodene or equivalent may be used.

5.16 Sodium Thiosulfate, Stock Solution, (0.75 N): Dissolve 186.14 g $Na_2S_2O_3 \cdot 5H_2O$ in boiled and cooled distilled water and dilute to 1 liter. Preserve by adding 5 ml chloroform.

5.17 Sodium Thiosulfate Standard Titrant, (0.0375 N): Prepare by diluting 50.0 ml of stock solution (5.16) to 1.0 liter. Preserve by adding 5 ml of chloroform. Standardize with 0.0375 N potassium biiodate (5.19, 5.23).

5.18 Sodium Thiosulfate Working Standard (0.0075 N): Transfer 100 ml of sodium thiosulfate standard titrant (5.17) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.19 Potassium Biiodate Standard, (0.0375 N): Dissolve 4.873 g potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liter. Dilute 250 ml to 1.0 liter for 0.0375 N biiodate solution.

5.20 Starch Solution: Prepare an emulsion of 10 g of soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator. Commercially available dry, powdered starch indicators may be used in place of starch solution.

5.21 Nitrogen Gas: Cylinder

5.22 Potassium Fluoride ($KF \cdot 2H_2O$): ACS Reagent Grade

5.23 Standardization of 0.0375 N Phenylarsine Oxide and 0.0375 N Sodium Thiosulfate: Dissolve approximately 2 g (± 1.0 g) KI (5.7) in 100 to 150 ml distilled water; add 10 ml H_2SO_4 solution (5.12) followed by 20 ml standard potassium biiodate solution (5.19). Place in dark for 5 minutes, dilute to 300 ml and titrate with the phenylarsine oxide (5.13) or sodium thiosulfate (5.17) to a pale straw color. Add a small scoop of indicator (5.15). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

6. Procedure

6.1 Pretreatment

6.1.1 Add a visible excess of CaO (5.5) to 400 ml of sample. Stir or shake vigorously for approximately 5 minutes. Filter through a dry, moderately retentive filter paper, discarding the first 75 ml.

6.2 Iodine Determination

6.2.1 Place 100 ml of pretreated sample (6.1) or a fraction thereof diluted to that volume, into a 150 ml beaker. Add a Teflon-coated stirring bar and place on a magnetic stirrer. Insert a pH electrode and adjust the pH to approximately 7 or slightly less by the dropwise addition of H_2SO_4 solution (5.12).

6.2.2 Transfer the sample to a 250 ml widemouthed conical flask. Wash beaker with small amounts of distilled water and add washings to the flask. A 250 ml iodine flask would increase accuracy and precision by preventing possible loss of the iodine generated upon addition of potassium iodide and sulfuric acid (6.4.1).

6.2.3 Add 15 ml sodium acetate solution (5.8) and 5 ml acetic acid solution (5.1). Mix well. Add 40 ml bromine water solution (5.2); mix well. Wait 5 minutes.

6.2.4 Add 2 ml sodium formate solution (5.10); mix well. Wait 5 minutes.

6.2.5 Purge space above sample with gentle stream of nitrogen (5.21) for approximately 30 seconds to remove bromine fumes.

6.2.6 If a precipitate forms (iron), add 0.5 g $KF \cdot 2H_2O$ (5.22).

6.2.7 A distilled water blank must be run with each set of samples because of iodide in reagents. If the blank is consistently shown to be zero for a particular "lot" of chemicals, it can be ignored.

6.2.8 Titrate as described in 6.4.

6.3 Bromide Plus Iodide Determination

6.3.1 Place 100 ml of pretreated sample (6.1) or a fraction thereof diluted to that volume, in a 150 ml beaker. Add 5 g NaCl and stir to dissolve. Neutralize by dropwise addition of HCl solution (5.6) as in (6.2.1). Transfer as in (6.2.2).

6.3.2 Add 20 ml of calcium hypochlorite solution (5.4). Add 1 ml of HCl solution (5.6) and add approximately 0.2 g calcium carbonate (5.3).

6.3.3 Heat to boiling on a hot plate; maintain boiling for 8 minutes.

6.3.4 Remove from hot plate and carefully add 4 ml sodium formate solution (5.10). Caution: TOO RAPID ADDITION MAY CAUSE FOAMING. Wash down sides with distilled water.

6.3.5 Return to hot plate and maintain boiling conditions for an additional 8 minutes. Occasionally wash down sides with distilled water if residue is deposited from boiling action.

6.3.6 Remove from hot plate. Wash down sides and allow to cool.

6.3.7 If a precipitate forms (iron), add 0.5 g $KF \cdot 2H_2O$ (5.22).

6.3.8 Add 3 drops sodium molybdate solution (5.11).

6.3.9 A distilled water blank must be run with each set of samples because of iodide, iodate, bromide, and/or bromate in reagents.

6.3.10 Titrate as described in 6.4.

6.4 Titration

6.4.1 Dissolve approximately 1 g potassium iodide (5.7) in sample from (6.2.8 or 6.3.10). Add 10 ml of H_2SO_4 solution (5.12) and place in dark for 5 minutes.

6.4.2 Titrate with standardized phenylarsine oxide working standard (5.14) or sodium thiosulfate working standard (5.18), adding indicator (5.15 or 5.20) as end point is approached (light straw color). Titrate to colorless solution. Disregard returning blue color.

7. Calculations

7.1 Principle: Iodide is determined by the titration of the sample as oxidized in (6.2): bromide plus iodide is determined by the titration of the sample as oxidized in (6.3). The amount of bromide is then determined by difference. The number of equivalents of iodine produced a constant of 13,320 as shown in the equation in (7.2). Experimental data is entered in the appropriate place and the equation is solved for mg/1 bromide.

7.2 Equation

$$\text{Br(mg/l)} = 13{,}320 \left[\left(\frac{A \times B}{C} \right) - \left(\frac{D \times E}{F} \right) \right]$$

where:

A = the number of ml of PAO needed to titrate the sample for bromide plus iodide (with the number of ml of PAO needed to titrate the blank subtracted).

B = the normality of the PAO needed to titrate the sample for bromide plus iodide.

C = the volume of sample taken (100 ml or a fraction thereof) to be titrated for bromide plus iodide.

D = the number of ml of PAO needed to titrate the sample for iodide (with the number of ml of PAO needed to titrate the blank subtracted). The blank for the iodide titration is often zero.

E = the normality of the PAO used to titrate the sample for iodide.

F = the volume of sample taken (100 ml or a fraction thereof) to be titrated for iodide.

8. Precision and Accuracy

8.1 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent, at concentrations of 0.3, 2.8, 5.3, 10.3 and 20.3 mg/1 of bromide, the standard deviations were ±0.13, ±0.37, ±0.38, ±0.44 and ±0.42 mg/1, respectively.

8.2 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent, at concentrations of 2.8, 5.3, 10.3 and 20.3 mg/1 of bromide, recoveries were 96, 83, 97 and 99%, respectively.

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1. Annual Book of ASTM Standards, Part 31, "Water", Standard D1246–68, Method C, p 328 (1976).
2. Bender, D. F., "Modification of the Iodimetric Titration Methods for the Determination of Bromide and its application to Mixed Domestic-Industrial Waste Effluents", Analyst (London), 100, p 400–404 (June 1975).

CHLORIDE

Method 325.1 (Colorimetric, Automated Ferricyanide AAI)

STORET NO. 00940

1. Scope and Application
   1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The applicable range is 1 to 250 mg Cl/1. Approximately 15 samples per hour can be analyzed.
2. Summary of Method
   2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in concentration proportional to the original chloride concentration.
3. Sample Handling and Preservation
   3.1 No special requirements.
4. Interferences
   4.1 No significant interferences.
5. Apparatus
   5.1 Technicon AutoAnalyzer consisting of:
      5.1.1 Sampler I.
      5.1.2 Continuous filter.
      5.1.3 Manifold.
      5.1.4 Proportioning pump.
      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 480 nm filters.
      5.1.6 Recorder.
6. Reagents
   6.1 Ferric Ammonium Sulfate: Dissolve 60 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$ in approximately 500 ml distilled water. Add 355 ml of conc. HNO_3 and dilute to 1 liter with distilled water. Filter.
   6.2 Saturated Mercuric Thiocyanate: Dissolve 5 g of $Hg(SCN)_2$ in 1 liter of distilled water. Decant and filter a portion of the saturated supernatant liquid to use as the reagent and refill the bottle with distilled water.
   6.3 Stock Solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140°C) NaCl in distilled water. Dilute to 1 liter in a volumetric flask. 1 ml = 0.5 mg Cl.
      6.3.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

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ml of Stock Solution	Conc., mg/l
1.0	5.0
2.0	10.0
4.0	20.0
8.0	40.0
15.0	75.0
20.0	100.0
30.0	150.0
40.0	200.0
50.0	250.0

7. Procedure
   7.1 No advance sample preparation is required. Set up manifold as shown in Figure 1. For water samples known to be consistently low in chloride content, it is advisable to use only one distilled water intake line.
   7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.
   7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.
   7.4 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.
   7.5 Switch sample line from distilled water to sampler and begin analysis.
8. Calculation
   8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.
9. Precision and Accuracy
   9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1, 100, and 250 mg Cl/1, the standard deviation was ±0.3.
   9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 10 and 100 mg Cl/1, recoveries were 97% and 104%, respectively.

Bibliography

1. J. E. O'Brien, "Automatic Analysis of Chlorides in Sewage", Waste Engr., 33, 670–672 (Dec. 1962).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 613, Method 602 (1975).

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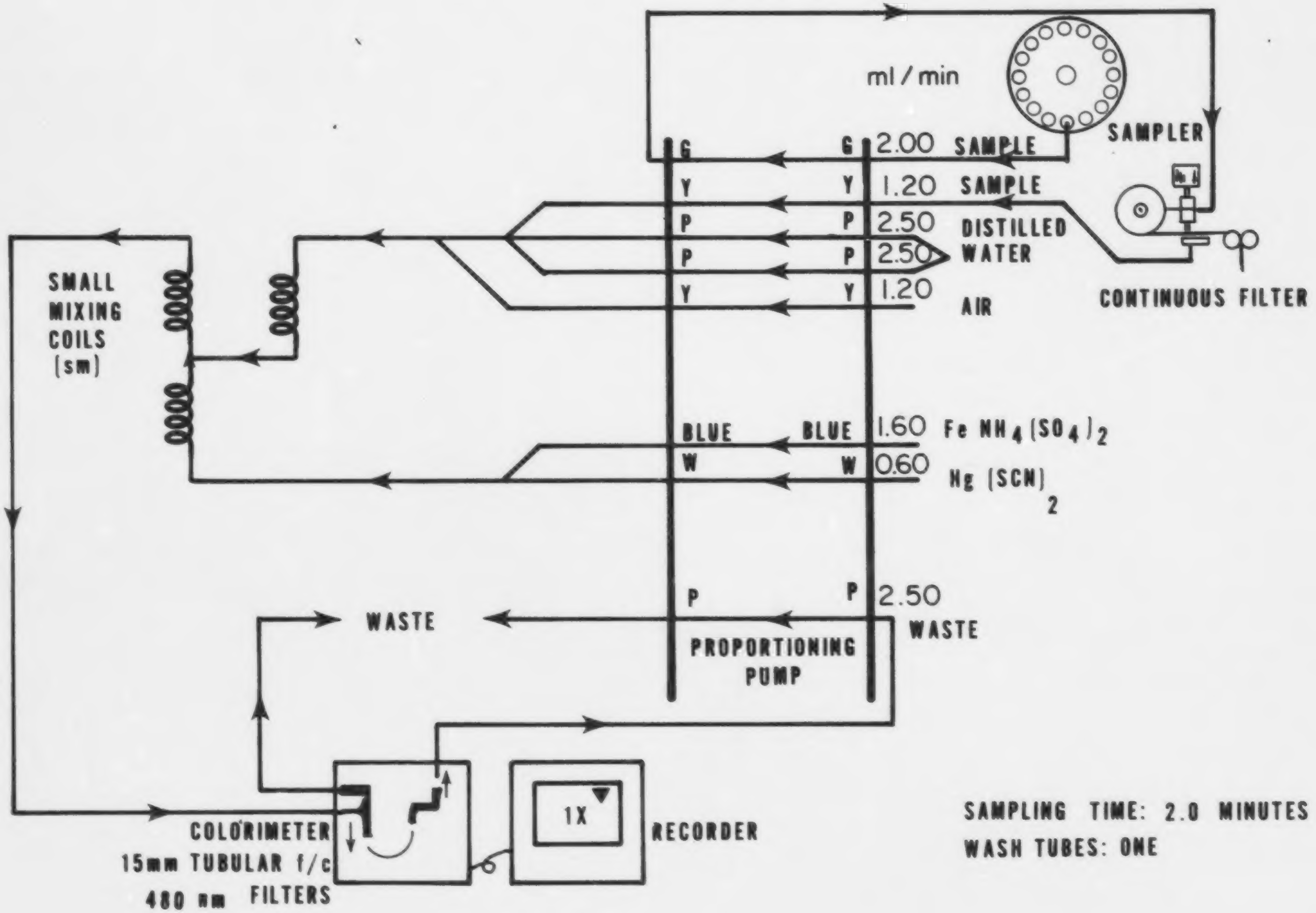
ml / min
SAMPLER
CONTINUOUS FILTER
G
G 2.00 SAMPLE
Y
Y 1.20 SAMPLE
P
P 2.50 DISTILLED
P
P 2.50 WATER
Y
Y 1.20 AIR
SMALL MIXING COILS (sm)
BLUE
BLUE 1.60 Fe NH$_4$(SO$_4$)$_2$
W
W 0.60 Hg (SCN)$_2$
P
P 2.50 WASTE
WASTE
PROPORTIONING PUMP
COLORIMETER
15mm TUBULAR f/c
480 nm FILTERS
1X
RECORDER

SAMPLING TIME: 2.0 MINUTES
WASH TUBES: ONE

FIGURE 1. CHLORIDE MANIFOLD AA-I

CHLORIDE

Method 325.2 (Colorimetric, Automated Ferricyanide AAII)

STORET NO. 00940

1. Scope and Application
   1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industral wastes. The applicable range is 1 to 200 mg Cl/1. This range may be extended by sample dilution. Approximately 30 samples per hour can be analyzed.
2. Summary of Method
   2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in concentration proportional to the original chloride concentration.
3. Sample Handling and Preservation
   3.1 No special requirements.
4. Interferences
   4.1 No significant interferences.
5. Apparatus
   5.1 Technicon AutoAnalyzer consisting of:
      5.1.1 Sampler.
      5.1.2 Continuous filter (optional).
      5.1.3 Analytical cartridge.
      5.1.4 Proportioning pump.
      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 480 nm filters.
      5.1.6 Recorder.
      5.1.7 Digital printer (optional).
6. Reagents
   6.1 Mercuric thiocyanate solution: Dissolve 4.17 gm of $Hg(SCN)_2$ in 500 ml of methanol. Dilute to 1 liter with methanol, mix and filter through filter paper.
   6.2 Ferric nitrate solution, 20.2%: Dissolve 202 gm of $Fe(NO_3)_3 \bullet 9\,H_2O$ in 500 ml of distilled water. Add 31.5 ml conc nitric acid, mix and dilute to 1 liter with distilled water.
   6.3 Color reagent: Add 150 ml of mercuric thiocyanate solution (6.1) to 150 ml of ferric nitrate solution (6.2), mix, and dilute to 1 liter with distilled water.
   6.4 Stock Solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140°C) NaCl in distilled water. Dilute to 1 liter in a volumetric flask. 1 ml = 0.5 mg Cl.
      6.4.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

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ml of Stock Solution	Conc., mg/l
1.0	5.0
2.0	10.0
4.0	20.0
8.0	40.0
15.0	75.0
20.0	100.0
30.0	150.0
40.0	200.0

7. Procedure

7.1 Where particulate matter is present, the sample must be filtered prior to the determination. This can be accomplished by having the Technicon continuous filter as an integral part of the system. The sample may be centrifuged in place of filtration.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line.

7.3 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.

7.4 When a stable baseline has been obtained, start the sampler.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

Bibliography

1. J. E. O'Brien, "Automatic Analysis of Chlorides in Sewage", Waste Engr., 33, 670–672 (Dec. 1962).
2. Technicon AutoAnalyzer II, Industrial Method No. 99–70W, Technicon Industrial Systems, Tarrytown, N. Y., 10591 (Sept. 1973).

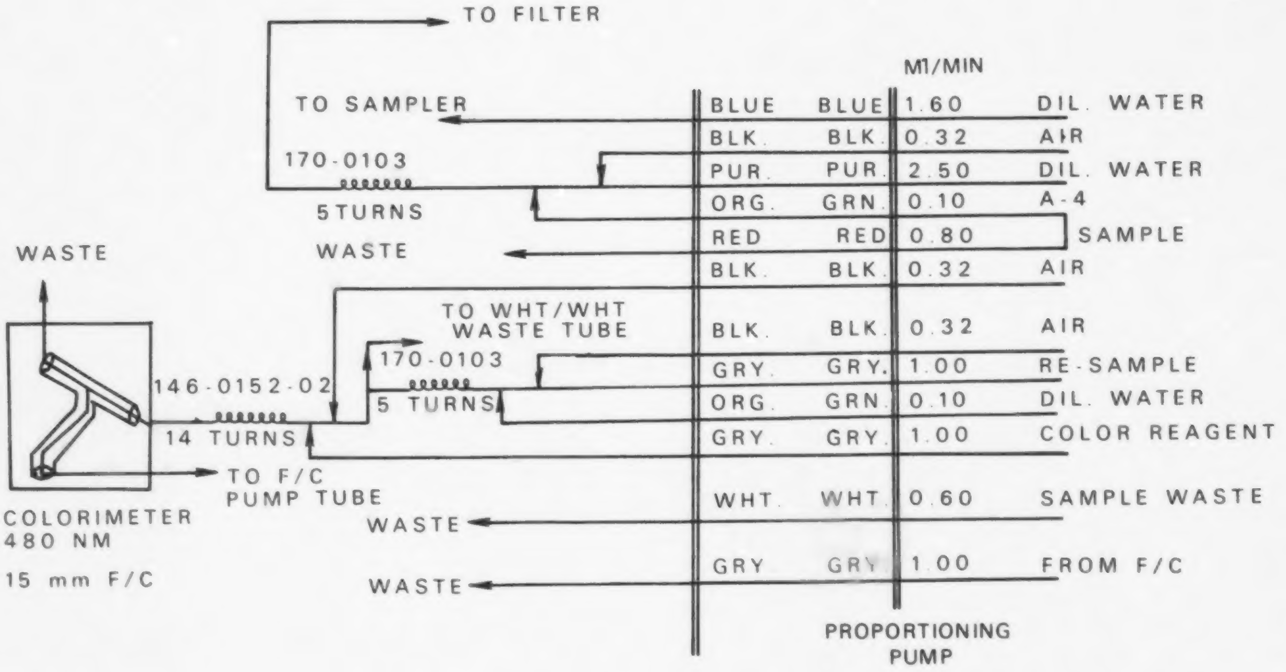
TO FILTER
M1/MIN
TO SAMPLER
170-0103
5TURNS
WASTE
WASTE
BLUE BLUE 1.60 DIL. WATER
BLK. BLK. 0.32 AIR
PUR. PUR. 2.50 DIL. WATER
ORG. GRN. 0.10 A-4
RED RED 0.80 SAMPLE
BLK. BLK. 0.32 AIR
TO WHT/WHT WASTE TUBE
BLK. BLK. 0.32 AIR
170-0103
5 TURNS
GRY. GRY. 1.00 RE-SAMPLE
ORG. GRN. 0.10 DIL. WATER
GRY. GRY. 1.00 COLOR REAGENT
146-0152-02
14 TURNS
TO F/C PUMP TUBE
COLORIMETER
480 NM
15 mm F/C
WHT. WHT. 0.60 SAMPLE WASTE
WASTE
GRY GRY 1.00 FROM F/C
WASTE
PROPORTIONING PUMP

FIGURE 1
CHLORIDE MANIFOLD AA 11

CHLORIDE

Method 325.3 (Titrimetric, Mercuric Nitrate)

STORET NO. 00940

1. Scope and Application
    1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
    1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volume, a sample aliquot containing not more than 10 to 20 mg Cl per 50 ml is used.
    1.3 Automated titration may be used.
2. Summary of Method
    2.1 An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.
3. Comments
    3.1 Anions and cations at concentrations normally found in surface waters do not interfere.
    3.2 Sulfite interference can be eliminated by oxidizing the 50 ml of sample solution with 0.5 to 1 ml of H_2O_2.
4. Apparatus
    4.1 Standard laboratory titrimetric equipment including a 1 ml or 5 ml microburet with 0.01 ml graduations.
5. Reagents
    5.1 Standard sodium chloride, 0.025 N: Dissolve 1.4613 g ± 0.0002 g sodium chloride (dried at 600 °C for 1 hour) in chloride-free water in a 1 liter volumetric flask and dilute to the mark 1 ml = 886.5 μg Cl.
    5.2 Nitric acid, HNO_3 solution (3 + 997)
    5.3 Sodium hydroxide solution, NaOH, (10 g/1)
    5.4 Hydrogen peroxide (30%), H_2O_2
    5.5 Hydroquinone solution (10 g/liter): Dissolve 1 g of purified hydroquinone in water in a 100 ml volumetric and dilute to the mark.
    5.6 Mercuric nitrate titrant (0.141 N): Dissolve 25 g $Hg(NO_3)_2 \cdot H_2O$ in 900 ml of distilled water acidified with 5.0 ml conc. HNO_3 in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.141 N and check. Store in a dark bottle. A 1.00 ml aliquot is equivalent to 5.00 mg of chloride.
    5.7 Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g $Hg(NO_3)_2 \cdot H_2O$ in 50 ml of distilled water acidified with 0.5 ml conc. HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard

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sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.025 N and check. Store in a dark bottle.

5.8 Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g $Hg(NO_3)_2{\bullet}H_2O$ in 25 ml of distilled water acidified with 0.25 ml of conc. HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1 ml aliquot is equivalent to 500 *u*g of chloride.

5.9 Mixed indicator reagent: Dissolve 0.5 g crystalline diphenylcarbazone and 0.05 g bromophenol blue powder in 75 ml 95% ethanol in a 100 ml volumetric flask and dilute to the mark with 95% ethanol. Store in brown bottle and discard after 6 months.

5.10 Xylene cyanole FF solution: Dissolve 0.005 g of xylene cyanole FF dye in 95% ethanol or isopropanol in a 100 ml volumetric and dilute to the mark with 95% ethanol or isopropanol.

6. Procedure

6.1 Use 50 ml of sample or an aliquot of sample diluted to 50 ml with distilled water, so that the concentration of chloride does not exceed 20 mg/aliquot. If the sample or aliquot contains more than 2.5 mg of chloride, use 0.025N mercuric nitrate titrant (5.7) in step 6.6. If the sample or aliquot contains less than 2.5 mg of chloride, use 0.0141N mercuric nitrate titrant (5.8) in step 6.6. Determine an indicator blank on 50 ml chloride-free water using step 6.6. If the sample contains less than 0.1 mg/l of chloride concentrate an appropriate volume to 50 ml.

6.2 Add 5 drops of mixed indicator reagent (5.9), shake or swirl solution.

6.3 If a blue-violet or red color appears add HNO_3 solution (5.2) dropwise until the color changes to yellow.

6.4 If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (5.3) dropwise until the color changes to blue-violet; then add HNO_3 solution (5.2) dropwise until the color changes to yellow.

6.5 Add 1 ml excess HNO_3 solution (5.2).

6.6 Titrate with 0.025 N mercuric nitrate titrant (5.7) until a blue-violet color persists throughout the solution. See 6.1 for choice of titrant normality. Xylene cyanol FF solution (5.10) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.

6.7 Additional steps to eliminate particular interferences:

6.7.1 If chromate is present and iron is not present the end point may be difficult to detect.
be an olive-purple color.

6.7.2 If chromate is present at > 100 mg/1 and iron is not present, add 2 ml of fresh hydroquinone solution (5.5).

6.7.3 If ferric ion is present use volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 ml fresh hydroquinone solution (5.5).

6.7.4 If sulfite ion is present, add 0.5 ml of H_2O_2 solution (5.4) to 50 ml sample and mix for 1 minute.

7. Calculation

$$\text{mg chloride/l} = \frac{(A - B)N \times 35{,}450}{\text{ml of sample}}$$

where:
A = ml titrant for sample
B = ml titrant for blank
N = normality mercuric nitrate titrant

mg NaCl/l = mg chloride/l x 1.65

8. Precision and Accuracy

8.1 Forty two analysts in eighteen laboratories analyzed synthetic water samples containing exact increments of chloride, with the following results:

Increment as Chloride mg/liter	Precision as Standard Deviation mg/liter	Accuracy as	
		Bias, %	Bias, mg/liter
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	−0.51	−0.5
382	11.70	−0.61	−2.3
398	11.80	−1.19	−4.7

(FWPCA Method Study 1, Mineral and Physical Analyses)

8.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 34 mg Cl/1, the standard deviation was ±1.0.

8.3 A synthetic unknown sample containing 241 mg/1 chloride, 108 mg/1 Ca, 82 mg/1 Mg, 3.1 mg/1 K, 19.9 mg/1 Na, 1.1 mg/1 nitrate N, 0.25 mg/1 nitrite N, 259 mg/1 sulfate and 42.5 mg/1 total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

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1. Annual Book of ASTM Standards, Part 31, "Water", Standard D512–67, Method A, p 270 (1976).

CHLORINE, TOTAL RESIDUAL

Method 330.1 (Titrimetric, Amperometric)

STORET NO. 50060

1. Scope and Application
   1.1 The amperometric titration method is applicable to all types of waters and wastes that do not contain a substantial amount of organic matter.
2. Summary of Method
   2.1 Chlorine (hypochlorite ion, hypochlorous acid) and chloramines stoichiometrically liberate iodine from potassium iodide at pH 4 or less.
   2.2 The iodine is titrated with standard reducing agent such as sodium thiosulfate or phenylarsine oxide using an amperometer to determine the end point.
   2.3 The results are calculated as mg/1 Cl even though the actual measurement is of total oxidizing power because chlorine is the dominant oxidizing agent present.
3. Interferences
   3.1 Manganese, nitrite and iron do not interfere.
   3.2 Stirring can lower chlorine values by volatilization.
   3.3 If dilution is necessary, it must be done with distilled water which is free of chlorine, chlorine-demand and ammonia.
   3.4 Copper and silver poison the electrode.
4. Apparatus
   4.1 An amperometer consisting of a microammeter with necessary electrical accessories, a cell unit with a salt bridge, reference electrode and an agitator: Commercially available. If the entire system (including titrant delivery system) is to be used, make sure that the volume read off the pipet or buret is really being delivered to the sample cell. Reservoir-type system sometimes back up, producing false readings.
   4.2 A microburet, 0–2 ml or 0–10 ml, depending on required precision, accuracy and range.
5. Reagents
   5.1 Phenylarsine oxide solution (0.00564N), commercially available, Wallace and Tiernan or equivalent. Standardize with potassium biiodate (5.8, 5.9).
   5.2 Potassium Iodide, KI, crystals.
   5.3 Potassium Iodide Solution: Dissolve 50 g KI in freshly boiled and cooled distilled water and dilute to 1 liter. Store in colored, glass-stoppered bottle in refrigerator. Discard when yellow color develops.
   5.4 Commercially available starch indicators such as thyodene or equivalent may be used.
   5.5 Acetate buffer solution (pH 4): Dissolve 146g anhydrous $NaC_2H_3O_2$ or 243g $NaC_2H_3O_2 \cdot 3H_2O$ in 400 ml distilled water, add 480g conc acetic acid and dilute to 1 liter with distilled water.

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5.6 Sulfuric Acid (1:4): Slowly add 200 ml H_2SO_4 (sp. gr. 1.84) to 800 ml of distilled water.

5.7 Potassium biiodate (0.1N): Dissolve 3.249g potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liters. Store in a glass stoppered bottle.

5.8 Potassium biiodate (0.005N): Dilute 50 ml of 0.1N potassium biiodate (5.7) to 1-liter in a volumetric flask. Store in a glass stoppered bottle.

5.9 Standardization of 0.00564N phenylarsine oxide: Dissolve approximately 2g (±1g) KI (5.2) in 100 to 150 ml distilled water; add 10 ml H_2SO_4 solution (5.6) followed by 20 ml 0.005N potassium biiodate solution (5.8). Place in dark for 5 minutes; dilute to 300 ml and titrate with 0.00564N phenylarsine oxide solution (5.1) to a pale straw color. Add a small scoop of indicator (5.4). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

$$\text{N PAO} = \frac{20 \times 0.005}{\text{ml PAO}}$$

Adjust PAO solution if necessary and recheck.

6. Procedure

6.1 Place 200 ml of sample in the sample container. This volume is convenient because the buret reading in milliliters is equivalent to mg/l Cl. Up to 2 mg/l is reliably titrated this way. Smaller sample aliquots diluted to 200 ml are used for concentrations greater than 2 mg/l. The construction of the cell and electrode component usually require 200 ml of sample.

6.2 Place on electrode assembly.

6.3 Add 1.0 ml KI solution (5.3).

6.4 Add 1 ml acetate buffer (5.5).

6.5 Titrate with 0.00564N PAO (5.1).

6.6 As each increment is added the needle deflects toward rest. When the needle no longer deflects subtract the last drop added from the buret reading to obtain the mg/l Cl. Less and/or slower deflection signals that the end point is near.

7. Calculations

7.1 For 0.00564N PAO and a 200 ml sample there are no calculations. The buret reading is in mg/l. The last increment, when the needle does not deflect toward rest, must be subtracted.

8. Precision and Accuracy

8.1 More than 20 laboratories analyzed prepared samples of 0.64 and 1.83 mg/l total Cl. The relative standard deviations were 24.8% and 12.5% respectively and the relative errors were 8.5% and 8.8% respectively.

In a single operator, single laboratory situation the following results were obtained.

Sample Matrix	Average mg/l	Stand Dev. mg/l	Rel. Stand. Dev. %
Distilled Water	0.38	0.02	6.1
	3.50	0.01	0.2
Drinking Water	0.97	0.03	2.6
River Water	0.57	0.02	3.0
Domestic Sewage	0.41	0.03	6.9

For these samples the results were compared to the iodometric titration as a means of obtaining a relative accuracy.

Sample Matrix	Iodometric Titration mg/l	Amperometric Titration mg/l	% Recovery
Drinking Water	0.94	0.97	103.2
River Water	0.56	0.57	101.8
Domestic Sewage	0.50	0.41	82.0

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 322, Method 409C (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1253–76, p 277, Method A (1976).
3. Bender, D. F., "Comparison of Methods for the Determination of Total Available Residual Chlorine in Various Sample Matrices", EPA Report-600/4–78–019.

CHLORINE, TOTAL RESIDUAL

Method 330.2 (Titrimetric, Back, Iodometric)
(Starch or Amperometric Endpoint)

STORET NO. 50060

1. Scope and Application
   1.1 The iodometric backtitration method is applicable to all types of waters but is primarily used for wastewater because it eliminates any contact between the full concentration of liberated iodine and the wastewater.
2. Summary of Method
   2.1 Chlorine (hypochlorite ion, hypochlorous acid) and chloramines stoichiometrically liberate iodine from potassium iodide at pH 4 or less.
   2.2 The iodine immediately quantitatively oxidizes a standardized reducing agent such as sodium thiosulfate or phenylarsine oxide.
   2.3 The excess reducing agent is then determined by titrating with a standard iodine titrant. The starch endpoint color change is from clear to blue.
   2.4 A subtraction of the excess amount of reducing agent is included in the calculations and the results are reported as mg/1 Cl even though the actual measurement is of total oxidizing power because chlorine is the dominant oxidizing agent present.
3. Interferences
   3.1 Manganese, iron and nitrite interference may be minimized by buffering to pH 4 before the addition of KI.
   3.2 High concentrations of organics may cause uncertainty in the endpoint. This uncertainty can be reduced by acidifying to pH 1.0 if manganese, iron and nitrite are absent.
   3.3 Turbidity and color may make the endpoint difficult to detect. Practice runs with spiked samples may be necessary.
4. Apparatus
   4.1 Standard laboratory glassware is used. A microburet 0–2 ml or 0–10 ml is used depending on the desired range and accuracy.
5. Reagents
   5.1 Phenylarsine oxide solution (0.00564N): Wallace and Tierman or equivalent. Standardize with potassium biiodate (5.6, 5.9).
   5.2 Acetate buffer solution (pH 4): Dissolve 146 g anhydrous $NaC_2H_3O_2$ or 243 g $NaC_2H_3O_2 \cdot 3H_2O$ in 400 ml distilled water, add 480 g conc acetic acid and dilute to 1 liter with distilled water.
   5.3 Standard iodine solution (0.1N): Dissolve 40 g KI in 25 ml distilled water, add 13 g resublimed iodine and stir until dissolved. Transfer to a 1 liter volumetric flask and dilute to the mark. Determine the exact normality (5.11).

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5.4 Standard iodine titrant (0.0282N): Dissolve 25 g KI in a little distilled water in a 1 liter volumetric flask. Add the calculated amount of 0.1N standard iodine (5.3) to produce a 0.0282N solution. Standardize daily (5.12). Store in amber bottle or in dark; protect from sunlight at all times and keep from contact with rubber.

5.5 Potassium biiodate (0.1N): Dissove 3.249g potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liter. Store in a glass stoppered bottle.

5.6 Potassium biiodate (0.005N): Dilute 50 ml of 0.1N potassium biiodate (5.5) to 1 liter in a volumetric flask. Store in glass stoppered bottle.

5.7 Commercially available starch indicators such as thyodene or equivalent may be used.

5.8 Sulfuric Acid Solution (1:4): Slowly add 200 ml H_2SO_4 (sp. gr. 1.84) to 800 ml of distilled water.

5.9 Standardization of 0.00564N phenylarsine oxide: Dissolve approximately 2g (±1g) KI in 100 to 150 ml distilled water; add 10 ml H_2SO_4 solution (5.8) followed by 20 ml 0.005N potassium biiodate solution (5.6). Place in dark for 5 minutes; dilute to 300 ml and titrate with 0.00564N phenylarsine oxide solution (5.1) to a pale straw color. Add a small scoop of indicator (5.7). Wait until homogenous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

$$\text{N PAO} = \frac{20 \times 0.005}{\text{ml PAO}}$$

Adjust PAO solution if necessary and recheck.

5.10 Standardization of 0.0375N phenylarsine oxide: Dissolve approximately 2 g (±1g) KI in 100 to 150 ml distilled water; add 10 ml H_2SO_4 solution (5.8) followed by 20 ml 0.1N potassium biiodate solution (5.5). Place in dark for 5 minutes, dilute to 300 ml and titrate with 0.0375N phenylarsine oxide solution (5.10) to a pale straw color. Add a small scoop of indicator (5.7). Wait until homogenous blue color develops and continue the titration, drop by drop until the color disappears. Run in duplicate. Duplicate determination should agree within ±0.05 ml.

$$\text{N PAO} = \frac{20 \times 0.1}{\text{ml PAO}}$$

Adjust PAO solution if necessary and recheck.

5.11 Standardization of 0.1N Iodine solution: Dissolve approximately 2g (±1.g) KI in 100 to 150 ml distilled water; add 20 ml Iodine Solution (5.3). Dilute to 300 ml and titrate with 0.0375N phenylarsine oxide solution (5.10) to a pale straw color. Add a small scoop of indicator (5.7). Wait until homogenous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

$$N_{I_2} = \frac{\text{ml PAO} \times 0.0375}{20}$$

Adjust iodine solution if necessary and recheck.

5.12 Standardization of 0.0282N Iodine solution: Dissolve approximately 2 g (±1.g) KI in 100 to 150 ml distilled water; add 20 ml Iodine solution (5.4). Dilute to 300 ml and titrate with 0.0375N phenylarsine oxide solution (5.10) to a pale straw color. Add a small scoop of indicator (5.7). Wait until homogenous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

$$N_{I_2} = \frac{\text{ml PAO} \times 0.0375}{20}$$

Adjust iodine solution if necessary and recheck.

6. Procedure

6.1 Starch-Iodide End Point

6.1.1 Place 5.00 ml of 0.00564N PAO solution (5.9) in a flask.
6.1.2 Add approximately 1g KI on a scoop.
6.1.3 Add 4 ml acetate buffer solution (5.2).
6.1.4 Add 200 ml of sample. For concentrations above 10 mg/1, a sample of less volume may be diluted to 200 ml wth chlorine-free, chlorine demand-free distilled water.
6.1.5 Mix well.
6.1.6 Add approximately 4 mg indicator (5.7) just before titration.
6.1.7 Titrate with 0.0282N iodine solution (5.12) to the first appearance of a blue color that persists after mixing. Record the ml of titrant used.

6.2 Amperometric End Point

6.2.1 Perform steps 6.1.1–6.1.5 inclusive or follow the directions of the manufacturer of the amperometric titrator. Prepackaged reagents should be checked (restandardized).
6.2.2 Place the solution in the proper position on the amperometric titrater.
6.2.3 Titrate with 0.0282N Iodine Solution (5.12) Observe the response of the meter needle. Initially the needle will remain stationary. As the endpoint is approached the needle will temporarily deflect, then return to or near to its original position. Continue dropwise. When the needle deflects and remains deflected the end point has been exceeded by one drop. Subtract 1/20th of an ml from the buret reading and record the result.

7. Calculations

$$\text{mg/l Cl} = \frac{(A - 5B) \times 200}{C}$$

where:

A = ml 0.00564 N PAO

B = ml 0.0282 N I_2

C = ml sample

8. Precision and Accuracy

8.1 Starch-Iodine Endpoint

8.1.1 Precision

In a single operator, single laboratory situation the following results were obtained.

Sample Matrix	Average mg/l	Stand. Dev. ±mg/l	Rel. Stand. Dev. %
Distilled Water[a]	0.41	0.05	12.2
	3.51	0.12	3.3
Drinking Water	0.84	0.04	4.3
River Water	0.84	0.02	2.7
Domestic Sewage[b]	0.87	0.07	7.6
Raw Sewage	0.55	0.09	16.0

[a] Three replicates for distilled water. Seven replicates for other sample matrices

[b] Secondary treatment

8.1.2 Accuracy (Relative)

For four samples the results were compared to the iodometric titration as a means of obtaining a relative accuracy.

Iodometric Sample Matrix	Starch Titration mg/l	Iodide Back Titration mg/l	% Recovery
Drinking Water	0.85	0.84	98.8
River Water	0.78	0.84	107.7
Domestic Sewage	1.00	0.87	87.0
Raw Sewage	Approx 0.5	0.55	Approx 100.0

8.2 Amperometric End Point

8.2.1 Precision

In a single operator, single laboratory situation the following results were obtained.

Sample Matrix	Average mg/l	Stand. Dev. ±mg/l	Rel. Stand. Dev. %
Distilled Water[a]	0.58	0.05	8.8
	3.53	0.07	2.0
Drinking Water	0.82	0.05	5.9
River Water	0.68	0.06	9.4
Domestic Sewage[b]	1.10	0.09	8.3

[a] Three replicates for distilled water. Seven replicates for other sample matrices.

[b] Secondary treatment.

8.2.2 Accuracy

For three samples the results were compared to the iodometric titration as a means of obtaining a relative accuracy.

Sample Matrix	Iodometric Titration mg/l	Amperometric Back Titration mg/l	% Recovery
Drinking Water	0.83	0.82	98.8
River Water	0.66	0.68	103.0
Domestic Sewage	1.45	1.10	75.7

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Ed., p. 318, Method 409B "Iodometric Method II", (1975).
2. ASTM Standards, Part 31 "Water", p. 276, Method D1253–76 (1976).
3. Bender, D. F., "Comparison of Methods for the Determination of Total Available Residual Chlorine in Various Sample Matrices", EPA Report-600/4–78–019.

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CHLORINE, TOTAL RESIDUAL

Method 330.3 (Titrimetric, Iodometric)

STORET NO. 50060

1. Scope and Application
    1.1 The iodometric titration method is applicable to natural and treated waters at concentrations greater than 0.1 mg/l.
2. Summary of Method
    2.1 Chlorine (hypochlorite ion, hypochlorous acid) and chloramines stoichiometrically liberate iodine from potassium iodide at pH 4 or less.
    2.2 The iodine is titrated with a standard reducing agent such as sodium thiosulfate or phenylarsine oxide using a starch indicator.
    2.3 The results are calculated as mg/1 Cl even though the actual measurement is of total oxidizing power because chlorine is the dominant oxidizing agent present.
3. Interferences
    3.1 Ferric, manganic and nitrite ions interfere, the neutral titration minimizes these interferences.
    3.2 Acetic acid is used for the acid titration. Sulfuric acid may be used if no interferences are present. Hydrochloric acid should never be used.
    3.3 Turbidity and color may make the endpoint difficult to detect. Practice runs with spiked samples may be necessay.
4. Apparatus
    4.1 Standard laboratory glassware is used. A microburet 0–2 ml or 0–10 ml is used depending on the desired range and accuracy.
5. Reagents
    5.1 Acetic acid, conc (glacial)
    5.2 Potassium iodide, KI, crystals
    5.3 Phenylarsine oxide (0.00564N): Wallace and Tiernan or equivalent. Standardize with potassium biiodate (5.8, 5.12).
    5.4 Phenylarsine oxide (0.0375N): Hach Chemical Co. or equivalent. Standardize with potassium biiodate (5.7, 5.13).
    5.5 Commercially available starch indicators such as thyodene or equivalent may be used.
    5.6 Potassium biiodate (0.1N): Dissolve 3.249 g potassium biiodate, previously dried two hours at 103°C, in distilled water and dilute to 1.0 liter. Store in a glass stoppered bottle.
    5.7 Potassium biiodate (0.05N): Dilute 500 ml of 0.1 N potassium biiodate (5.6) to 1 liter in a volumetric flask. Store in glass stoppered bottle.
    5.8 Potassium biiodate (0.005N): Dilute 50 ml of 0.1 N potassium biiodate (5.6) to 1 liter in a volumetric flask. Store in glass stoppered bottle.

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5.9 Standard iodine solution (0.1N): Dissolve 40 g KI in 25 ml distilled water, add 13 g resublimed iodine and stir until dissolved. Transfer to a 1 liter volumetric flask and dilute to the mark. Determine the exact normality (5.14).

5.10 Standard iodine titrant (0.0282N): Dissolve 25 g KI in a little distilled water in a 1 liter volumetric flask. Add the calculated amount of 0.1 N standard iodine to produce a 0.0282 N solution. Standardize daily (5.15). Store in amber bottle or in dark; protect from sunlight at all times and keep from contact with rubber.

5.11 Sulfuric acid solution (1:4): Slowly add 200 ml H_2SO_4 (sp. gr. 1.84) to 800 ml of distilled water.

5.12 Standardization of 0.00564N phenylarsine oxide: Dissolve approximately 2 g (±1 g) KI (5.2) in 100 to 150 ml distilled water; add 10 ml H_2SO_4 solution (5.11) followed by 20 ml 0.005 N potassium biiodate solution (5.8). Place in dark for 5 minutes, dilute to 300 ml and titrate with 0.00564N phenylarsine oxide solution (5.3) to a pale straw color. Add a small scoop of indicator (5.5). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determination should agree within ±0.05 ml.

$$\text{N PAO} = \frac{20 \times 0.005}{\text{ml PAO}}$$

Adjust PAO solution if necessary and recheck.

5.13 Standardization of 0.0375N phenylarsine oxide: Dissolve approximately 2 g (±1 g) KI (5.2) in 100 to 150 ml distilled water; add 10 ml H_2SO_4 solution (5.11) followed by 20 ml 0.05 N potassium biiodate solution (5.7). Place in dark for 5 minutes, dilute to 300 ml and titrate wth 0.0375 N phenylarsine oxide solution (5.4) to a pale straw color. Add a small scoop of indicator (5.5). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

$$\text{N PAO} = \frac{20 \times 0.1}{\text{ml PAO}}$$

Adjust PAO solution if necessary and recheck.

5.14 Standardization of 0.1 N iodine solution: Dissolve approximately 2 g (±1 g) KI (5.2) in 100 to 150 ml distilled water; add 20 ml iodine solution (5.9). Dilute to 300 ml and titrate with 0.0375 N phenylarsine oxide solution (5.4) to a pale straw color. Add a small scoop of indicator (5.5). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

$$N_{I_2} = \frac{\text{ml PAO} \times 0.0375}{20}$$

Adjust iodine solution if necessary and recheck.

5.15 Standardization of 0.0282N iodine solution: Dissolve approximately 2 g (±1 g) KI (5.2) in 100 to 150 ml distilled water; add 20 ml iodine solution (5.10). Dilute to 300 ml and titrate with 0.0375 N phenylarsine oxide solution (5.4) to a pale straw color. Add a small scoop of indicator (5.5). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

$$N_{I_2} = \frac{\text{ml PAO} \times 0.0375}{20}$$

Adjust iodine solution if necessary and recheck.

6. Procedure

6.1 This procedure gives a convenient direct reading (ml titrant = mg/l Cl) in the range of the microburet (0.5 ml to 2,5 or 10 ml). The sample volume and reagent normalities may be varied at the analyst's discretion.

6.2 Place 5 ml acetic acid in an Erlenmeyer flask containing a Teflon coated magnetic stirring bar.

6.3 Add about 1 g KI (5.2) estimated on a spatula.

6.4 Add 200 ml sample.

6.5 Place on magnetic stirrer under buret.

6.6 Titrate away from direct sunlight with 0.00564N PAO (5.3) to a pale straw color. Add a scoop of indicator (5.5). Wait until blue color is homogeneously distributed, continue titrating until blue color is discharged. The ml of PAO is equal to the mg/l Cl plus or minus the blank correction (6.7) if any.

6.7 Blank titration: Using distilled water in place of the sample perform steps 6.2–6.5, add a scoop of indicator. Perform either 6.7.1 or 6.7.2 depending on color development.

6.7.1 Blank titration A: If a blue color develops titrate with 0.00564N PAO (5.3) to the disappearance of the blue color and record the results.

6.7.2 Blank titration B: If no blue color develops titrate with 0.0282N iodine (5.10) until blue color appears. Back titrate with 0.00564N PAO (5.3) and record the difference as titration B.

7. Calculations

7.1 The ml of PAO titrant is equal to mg/l Cl under the volumes and concentrations described. The blank correction A (6.7.1) can be directly subtracted. The blank correction B (6.7.2), which is added, involves a factor of 5 (unless one substitutes 0.00564N iodine for the 0.0282N iodine). Normally the reagents are pure enough that the blank correction is insignificant and therefore unnecessary.

8. Precision and Accuracy

Thirty to thirty two laboratories analyzed prepared samples of 0.64, 0.84 and 1.83 mg/1. The relative standard deviations were 27.0%, 32.4% and 23.6% respectively and relative errors were 23.6%, 18.5%, and 16.7% respectively.

In a single operator, single laboratory, situation the following results were obtained.

Sample matrix	Average mg/l	Standard deviation ±mg/l	Rel. standard deviation %
Distilled Water[a]	0.25	0.001	0.23
	4.02	0.03	0.76
Drinking Water	0.68	0.04	5.2
River water	0.30	0.03	9.7
Domestic Sewage[b]	1.11	0.06	5.9
Raw sewage	0.48	0.09	18.0

[a] Three replicates for distilled water. Seven replicates for other sample matrices.

[b] Secondary treatment

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th ed. p. 316, Method 409A "Iodometric Method I" (1975).
2. ASTM Standards, Part 31, "Water", p. 276, Method D1253–76 (1976).
3. Bender, D. F., "Comparison of Methods for the Determination of Total Available Residual Chlorine in Various Sample Matrices", EPA Report-600/4–78–019.

CHLORINE, TOTAL RESIDUAL

Method 330.4 (Titrimetric, DPD-FAS)

STORET NO. 50060

1. Scope and Application
   1.1 The N,N-diethyl-p-phenylene diamine (DPD) – ferrous ammonium sulfate (FAS) titration method is applicable to natural and treated waters at concentrations above 0.1 mg/1 Cl.
2. Summary of Method
   2.1 Chlorine (hypochlorite ion, hypochlorous acid) and chloramines stoichiometrically liberate iodine from potassium iodide at pH 4 or less.
   2.2 The iodine is titrated with FAS using DPD as the indicator.
   2.3 The results are calculated as mg/1 Cl even though the actual measurement is of total oxidizing power because chlorine is the dominant oxidizing agent present.
3. Interferences
   3.1 Bromine, bromamine and iodine are interferences which are normally present in insignificant amounts.
   3.2 Oxidized manganese interferes but can be corrected by subtraction after performing a titration in the presence of sodium arsenite ($NaAsO_2$)
   3.3 Copper interferes but is accounted for (up to approximately 10 mg/1 copper) by incorporation of EDTA. The EDTA also retards deterioration of DPD due to oxidation and completely suppresses dissolved oxygen errors by preventing trace metal catalysis.
   3.4 Turbidity and color may make the endpoint difficult to detect. Practice runs with spiked samples may be necessary.
4. Apparatus
   4.1 Standard laboratory glassware is used. A microburet, 0–2 ml or 0–10 ml, depending on the concentration range expected, is used.
5. Reagents
   5.1 Phosphate buffer solution: Dissolve 24 g anhydrous disodium hydrogen phosphate, Na_2HPO_4, and 46 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, in distilled water. Dissolve 800 mg. disodium ethylenediamine tetraacetate dihydrate in 100 ml distilled water. Combine these two solutions and dilute to 1 liter with distilled water. Add 20 mg. $HgCl_2$ as a preservative.
   5.2 N,N-Diethyl-p-phenylenediamine (DPD) indicator solution: Dissolve 1 g DPD oxalate or 1.5 g p-amino-N,N-diethylaniline sulfate in chlorine free distilled water containing 8 ml of 1 + 3 H_2SO_4 and 200 mg disodium ethylenediamine tetraacetate dihydrate. Dilute to 1 liter, store in a colored, glass-stoppered bottle. Discard when discolored. The buffer and indicator sulfate are available as a combined reagent in stable powder form.
   CAUTION: The oxalate is toxic, avoid ingestion.

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5.3 Standard ferrous ammonium sulfate (FAS) titrant: Dissolve 1.106g Mohr's salt $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, in distilled water containing 1 ml of 1 + 3 H_2SO_4 (5.4) and make up to 1 liter with freshly boiled and cooled distilled water. Stable for one month. Check with titration by standard potassium dichomate (5.5). The FAS titrant is equivalent to 100 *ug* Cl/1.00 ml.

5.4 Sulfuric acid solution (1+3): Slowly add one part of H_2SO_4 (sp. gr. 1.84) to three parts of distilled water.

5.5 Potassium dichromate (0.1000N): Dissolve 4.904 g potassium dichromate ($K_2Cr_2O_7$) in distilled water and dilute to 1 liter.

5.6 Potassium Iodide, KI Crystals.

5.7 Sodium Arsenite Solution: Place 500 mg of sodium arsenite ($NaAsO_2$) in a flask and dilute to 100 ml with distilled water.

6. Procedure

6.1 This procedure gives a convenient direct reading (ml titrant = mg/1 Cl) up to 4 mg/1. An aliquot should be diluted to 100 ml if higher concentrations are present.

6.2 Place 5 ml of phosphate buffer (5.1) in a titration flask.

6.3 Add 5 ml of DPD indicator (5.2).

6.4 Add approximately 1 g of KI (5.6) on a scoop.

6.5 Add 100 ml of sample.

6.6 Wait 2 minutes.

6.7 Titrate with FAS (5.3) until the red color is discharged. Record the volume of titrant used.

6.8 If oxidized manganese is present

6.8.1 Place 5 ml of phosphate buffer (5.1) in a titration flask.

6.8.2 Add one small crystal of potassium iodide (5.6).

6.8.3 Add 0.5 ml of sodium arsenite solution (5.7).

6.8.4 Add 100 ml of sample. Mix.

6.8.5 Add 5 ml DPD indicator (5.2). Mix.

6.8.6 Titrate wth FAS (5.3) until the red color is discharged. Record the volume of titrant used.

7. Calculations

7.1 The ml of FAS titrant is equal to the mg/1 Cl. If oxidized manganese was present, subtract the amount of titrant used in 6.8.6 from the amount of titrant used in 6.7 to obtain the mg/1 Cl.

8. Precision and Accuracy

Nineteen laboratories analyzed prepared samples of 0.64 and 1.83 mg/1 Cl. The relative standard deviations were 19.2 and 9.4% respectively and the relative errors were 8.1 and 4.3% respectively.

In a single operator single laboratory situation the following results were obtained.

Sample Matrix	Average mg/l	Stand. Dev ±mg/l	Rel. Stnd. Dev %
Distilled Water[a]	0.34	0.02	5.6
	0.65	0.003	0.5
	3.45	0.02	0.5
Drinking Water	0.98	0.01	1.2
River Water	0.79	0.01	1.4
Domestic Sewage	1.08	0.02	1.8
Raw Sewage	0.79	0.03	3.3

[a] Three replicates for distilled water. Seven replicates for other samples.

For four samples the results were compared to the iodometric titration as a means of obtaining a relative accuracy.

Sample Matrix	Iodometric Titration mg/l	DPD FAS Titration mg/l	% Recovery
Drinking Water	0.91	0.98	107.7
River Water	0.73	0.79	108.2
Domestic Sewage	1.20	1.08	90.0
Raw Sewage	0.75	0.79	105.3

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Ed. Page 329, Method 409E, "DPD Ferrous Titrimetic Method" (1975).
2. Bender, D. F., "Comparison of Methods for the Determination of Total Available Residual Chlorine in Various Sample Matrices", EPA Report-600/4-78-019.

CHLORINE, TOTAL RESIDUAL

Method 330.5 (Spectrophotometric, DPD)

STORET NO. 50060

1. Scope and Application
   - 1.1 The DPD-Colorimetric method is applicable to natural and treated waters at concentrations from 0.2–4 mg/1.
2. Summary of Method
   - 2.1 Chlorine (hypochlorite ion, hypochlorous acid) and chloramines stoichiometrically liberate iodine from potassium iodide at pH 4 or less.
   - 2.2 The liberated iodine reacts with N,N-diethyl-p-phenylene diamine (DPD) to produce a red colored solution.
   - 2.3 The solution is spectrophotometrically compared to a series of standards, using a graph or a regression analysis calculation.
   - 2.4 The results are read or calculated into mg/1 Cl.
3. Interferences
   - 3.1 Any oxidizing agents; these are usually present at insignificant concentrations compared to the residual chlorine concentrations.
   - 3.2 Turbidity and color will essentially prevent the colorimetric analysis.
4. Apparatus
   - 4.1 Spectrophotometer for use at 515 nm and cells of light path 1 cm or longer.
5. Reagents
   - 5.1 Phosphate buffer solution: Dissolve 24 g anhydrous disodium hydrogen phosphate, Na_2HPO_4, and 46 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, in distilled water. Dissolve 800 mg disodium ethylenediamine tetraacetate dihydrate in 100 ml distilled water. Combine these two solutions and dilute to 1 liter with distilled water. Add 20 mg $HgCl_2$ as a preservative.
   - 5.2 N,N-Diethyl-p-phenylenediamine (DPD) indicator solution: Dissolve 1 g DPD oxalate or 1.5 g p-amino-N,N-diethylaniline sulfate in chlorine free distilled water containing 8 ml of 1 +3 H_2SO_4 (5.3) and 200 mg disodium ethylenediamine tetraacetate dihydrate. Dilute to 1 liter, store in a colored, glass-stoppered bottle. Discard when discolored. The buffer and indicator sulfate are available as a combined reagent in stable powder form. CAUTION: The oxalate is toxic, avoid ingestion.
   - 5.3 Sulfuric acid solution (1 + 3): Slowly add one part of H_2SO_4 (sp. gr. 1.84) to three parts of distilled water.
   - 5.4 Potassium Iodide, KI crystals.
   - 5.5 Stock Potassium Permanganate Solution: Place 0.891 g $KMnO_4$ in a volumetric flask and dilute to 1 liter.

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5.6 Standard Potassium Permanganate Solution: Dilute 10.00 ml of stock potassium permanganate solution (5.5) to 100 ml with distilled water in a volumetric flask. One milliliter of this solution diluted to 100 ml with distilled water is equivalent to 1.00 mg/1 Cl.

6. Procedure

6.1 Calibration

6.1.1 Prepare a series of permanganate standards covering the chlorine equivalent range of 0.05 to 4 mg/1.

6.1.2 Place 5 ml phosphate buffer (5.1) in a flask.

6.1.3 Add 5 ml DPD reagent (5.2).

6.1.4 Add 100 ml permanganate standard (6.1.1).

6.1.5 Read at 515 nm on a spectrophotometer and record the absorbance.

6.1.6 Return the contents of the cell to the flask.

6.1.7 Titrate the contents of the flask with standard ferrous ammonium sulfate (DPD-FAS Method), until the red color is discharged. Record the result.

6.2 Sample Analysis

6.2.1 Place 0.5 ml phosphate buffer (5.1) in flask.

6.2.2 Add 0.5 ml DPD reagent (5.2).

6.2.3 Add approximately 0.1 g KI (5.4).

6.2.4 Add 10 ml of sample.

6.2.5 Let stand 2 minutes.

6.2.6 Read at 515 nm on a spectrophotometer, and record the absorbance.

7. Calculations

7.1 Calibration Curve Method

7.1.1 Plot the absorbance of the standard permanganate solutions (6.1.5) on the vertical axis versus the titrated concentration (6.1.7) on the horizontal axis.

7.1.2 Draw the line of best fit through the points.

7.1.3 Locate the absorbance (6.2.6) of the sample on the vertical axis.

7.1.4 Read the concentration on the horizontal axis at the intersect of the absorbance and the calibration line.

7.2 Regression Analysis Calculation–Computerized

7.2.1 Enter the absorbance data of the standard permanganate solutions (6.1.5) and the respective titrated concentrations (6.1.7) in the appropriate places in the program.

7.2.2 Enter the absorbance data of the sample.

7.2.3 The computer will then display the concentration in mg/1 Cl.

8. Precision and Accuracy

Twenty-five laboratories analyzed prepared samples of 0.66 mg/1 Cl. The relative standard deviation was 27.6% and the relative error was 15.6%.

In a single laboratory, single operator situation the following results were obtained.

Sample Matrix	Average mg/l	Stnd. Dev. ± mg/l	Rel. Stnd. Dev. %
Distilled Water[a]	0.39	0.012	3.1
	3.61	0.11	3.2
Drinking Water	0.94	0.008	0.8
River Water	0.86	0.02	1.9
Domestic Sewage	1.07	0.03	2.4

[a] Three replicates for distilled water. Seven replicates for other samples.

For three samples the results were compared to the iodometric titration as a means of obtaining a relative accuracy.

Sample Matrix	Iodometric Titration mg/l	DPD Colorimetric mg/l	% Recovery
Drinking Water	0.86	0.94	109.3
River Water	0.70	0.86	122.9
Domestic Sewage	1.01	1.07	106.0

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2. Bender, D. F., "Comparison of Methods for the Determination of Total Available Residual Chlorine in Various Sample Matrices", EPA Report-600/4-78-019.

CYANIDES, AMENABLE TO CHLORINATION

Method 335.1 (Titrimetric; Spectrophotometric)

STORET NO. 00722

1. Scope and Application
    1.1 This method is applicable to the determination of cyanides amenable to chlorination in drinking, surface and saline waters, domestic and industrial wastes.
    1.2 The titration procedure is used for measuring concentrations of cyanide exceeding 1 mg/1 after removal of the cyanides amenable to chlorination. Below this level the colorimetric determination is used.
2. Summary of Method
    2.1 A portion of the sample is chlorinated at a $pH > 11$ to decompose the cyanide. Cyanide levels in the chlorinated sample are then determined by the method for Cyanide, Total, in this manual. Cyanides amenable to chlorination are then calculated by difference.
3. Reagents
    3.1 Calcium Hypochlorite solution: Dissolve 5 g of calcium hypochlorite ($Ca(OCl)_2$) in 100 ml of distilled water.
    3.2 Sodium Hydroxide solution: Dissolve 50 g of sodium hydroxide (NaOH) in distilled water and dilute to 1 liter.
    3.3 Ascorbic acid: crystals.
    3.4 Potassium Iodide–starch test paper.
4. Procedure
    4.1 Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500 ml aliquot or a volume diluted to 500 ml, add calcium hypochlorite solution (3.1) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide (3.2).

    Caution: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is recommended that this reaction be performed in a hood. For convenience, the sample may be agitated in a 1 liter beaker by means of a magnetic stirring device.
    4.2 Test for residual chlorine with KI-starch paper (3.4) and maintain this excess for one hour, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.
    4.3 After one hour, add 0.5 g portions of ascorbic acid (3.3) until KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to insure the presence of excess reducing agent.
    4.4 Test for total cyanide in both the chlorinated and unchlorinated aliquots as in the method Cyanide, Total, in this manual.

Approved for NPDES
Issued 1974

5. Calculation

5.1 Calculate the cyanide amendable to chlorination as follows:

$$CN, mg/l = A - B$$

where:

A = mg/l total cyanide in unchlorinated aliquot
B = mg/l total in chlorinated aliquot

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2036–75, Method B, p 505 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 376 and 370, Method 413F and D (1975).

CYANIDE, TOTAL

Method 335.2 (Titrimetric; Spectrophotometric)

STORET NO. 00720

1. Scope and Application

1.1 This method is applicable to the determination of cyanide in drinking, surface and saline waters, domestic and industrial wastes.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/1 (0.25 mg/250 ml of absorbing liquid).

1.3 The colorimetric procedure is used for concentrations below 1 mg/1 of cyanide and is sensitive to about 0.02 mg/1.

2. Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample Handling and Preservation

4.1 The sample should be collected in plastic or glass bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.

4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.06 g of ascorbic acid for each liter of sample volume.

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Issued 1974
Editorial revision 1974 and 1978
Technical Revision 1980

4.3 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample (pH $\geq$ 12) at the time of collection.

4.4 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1, 8.2 and 8.3.

5.2 Sulfides adversely affect the colorimetric and titration procedures. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation should be distilled by the optional procedure described in Procedure 8.2. The apparatus for this procedure is shown in Figure 3.

5.3 Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect.

5.3.1 Acidify the sample with acetic acid (1+9) to pH 6.0 to 7.0.
Caution: This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed.

5.3.2 Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with NaOH solution.

5.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation nitrate and nitrite will form nitrous acid which will react with some organic compounds to form oximes. These compounds formed will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 ml (for titration).

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

6.4 Reflux distillation apparatus for sulfide removal as shown in Figure 3. The boiling flask same as 6.1. The sulfide scrubber may be a Wheaton Bubber #709682 with 29/42 joints, size 100 ml. The air inlet tube should not be fritted. The cyanide absorption vessel should be the same as the sulfide scrubber. The air inlet tube should be fritted.

6.5 Flow meter, such as Lab Crest with stainless steel float (Fisher 11-164-50).

7. Reagents

7.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.2 Lead acetate: Dissolve 30 g of Pb $(C_2H_3O_2)\bullet 3H_2O$ in 950 ml of distilled water. Adjust the pH to 4.5 with acetic acid. Dilute to 1 liter.

7.5 Sulfuric acid; 18N: Slowly add 500 ml of concentrated H_2SO_4 to 500 ml of distilled water.

7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4\bullet H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 ml of distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 ml = 1 mg CN.

7.8 Standard cyanide solution, intermediate: Dilute 100.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 100.0 *u*g).

7.9 Working standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 10.0 ug CN.

7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 ml (1 ml = 1mg CN).

7.11 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 ml of acetone.

7.12 Chloramine T solution: Dissolve 1.0 g of white, water soluble Chloramine T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh daily.

7.13 Color Reagent — One of the following may be used:

7.13.1 Pyridine-Barbituric Acid Reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of conc. HCl, mix, and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 3,3'Dimethyl-1, 1'-diphenyl-[4,4'-bi-2 pyrazoline]-5,5'dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.

7.13.2.3 Pour solution (7.13.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.13.2.2) collecting the filtrate in the same container as filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.14 Magnesium chloride solution: Weight 510 g of $MgCl_2\bullet 6H_2O$ into a 1000 ml flask, dissolve and dilute to 1 liter with distilled water.

7.15 Sulfamic acid.

8. Procedure

8.1 For samples without sulfide.

8.1.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Pipet 50 ml of sodium hydroxide (7.1) into the absorbing tube. If the apparatus in Figure 1 is used, add distilled water until the spiral is covered. Connect the boiling flask, condenser, absorber and trap in the train. (Figure 1 or 2)

8.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enters the boiling flask through the air inlet tube. Proceed to 8.4.

8.2 For samples that contain sulfide.

8.2.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Pipet 50 ml of sodium hydroxide (7.1) to the absorbing tube. Add 25 ml of lead acetate (7.2) to the sulfide scrubber. Connect the boiling flask, condenser, scrubber and absorber in the train. (Figure 3) The flow meter is connected to the outlet tube of the cyanide absorber.

8.2.2 Start a stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately 1.5 liters per minute enters the boiling flask through the air inlet tube. The bubble rate may not remain constant while heat is being applied to the flask. It may be necessary to readjust the air rate occasionally. Proceed to 8.4.

8.3 If samples contain NO_3 and or NO_2 add 2 g of sulfamic acid solution (7.15) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

8.4 Slowly add 50 ml 18N sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 min. Pour 20 ml of magnesium chloride (7.14) into the air inlet and wash down with a stream of water.

8.5 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.6 Drain the solution from the absorber into a 250 ml volumetric flask. Wash the absorber with distilled water and add the washings to the flask. Dilute to the mark with distilled water.

8.7 Withdraw 50 ml or less of the solution from the flask and transfer to a 100 ml volumetric flask. If less than 50 ml is taken, dilute to 50 ml with 0.25N sodium hydroxide solution (7.4). Add 15.0 ml of sodium phosphate solution (7.6) and mix.

8.7.1 Pyridine-barbituric acid method: Add 2 ml of chloramine T (7.12) and mix. See Note 1. After 1 to 2 minutes, add 5 ml of pyridine-barbituric acid solution (7.13.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.7.2 Pyridine-pyrazolene method: Add 0.5 ml of chloramine T (7.12) and mix. See Note 1 and 2. After 1 to 2 minutes add 5 ml of pyridine-pyrazolone solution

(7.13.1) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read absorbance at 620 nm in a 1 cm cell.

NOTE 1: Some distillates may contain compounds that have a chlorine demand. One minute after the addition of chloramine T, test for residual chlorine with KI-starch paper. If the test is negative, add an additional 0.5 ml of chlorine T. After one minute, recheck the sample.

NOTE 2: More than 05. ml of chloramine T will prevent the color from developing with pyridine-pyrazolone.

8.8 Standard curve for samples without sulfide.

8.8.1 Prepare a series of standards by pipeting suitable volumes of standard solution (7.9) into 250 ml volumetric flasks. To each standard add 50 ml of 1.25 N sodium hydroxide and dilute to 250 ml with distilled water. Prepare as follows:

ML of Working Standard Solution (1 ml = 10 μg CN)	Conc. μg CN per 250 ml
0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

8.8.2 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree within ±10% of the undistilled standards the analyst should find the cause of the apparent error before proceeding.

8.8.3 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.8.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to 500 ml of sample to insure a level of 20 μg/l. Proceed with the analysis as in Procedure (8.1.1).

8.9 Standard curve for samples with sulfide.

8.9.1 It is imperative that all standards be distilled in the same manner as the samples. Standards distilled by this method will give a linear curve, but as the concentration increases, the recovery decreases. It is recommended that at least 3 standards be distilled.

8.9.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.10 Titrimetric method.

8.10.1 If the sample contains more than 1 mg/l of CN, transfer the distillate or a suitable aliquot diluted to 250 ml, to a 500 ml Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.10.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.10.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples.

9. Calculation

9.1 If the colorimetric procedure is used, calculate the cyanide, in *ug*/1, in the original sample as follows:

$$\text{CN}, ug/\text{l} = \frac{A \times 1{,}000}{B} \times \frac{50}{C}$$

where:

A = *ug* CN read from standard curve
B = ml of original sample for distillation
C = ml taken for colorimetric analysis

9.2 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/l} = \frac{(A - B)1{,}000}{\text{ml orig. sample}} \times \frac{250}{\text{ml of aliquot titrated}}$$

where:

A = volume of $AgNO_3$ for titration of sample.
B = volume of $AgNO_3$ for titration of blank.

10. Precision and Accuracy

10.1 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28 and 0.62 mg/1 CN, the standard deviations were ±0.005, ±0.007, ±0.031 and ±0.094, respectively.

10.2 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/1 CN, recoveries were 85% and 102%, respectively.

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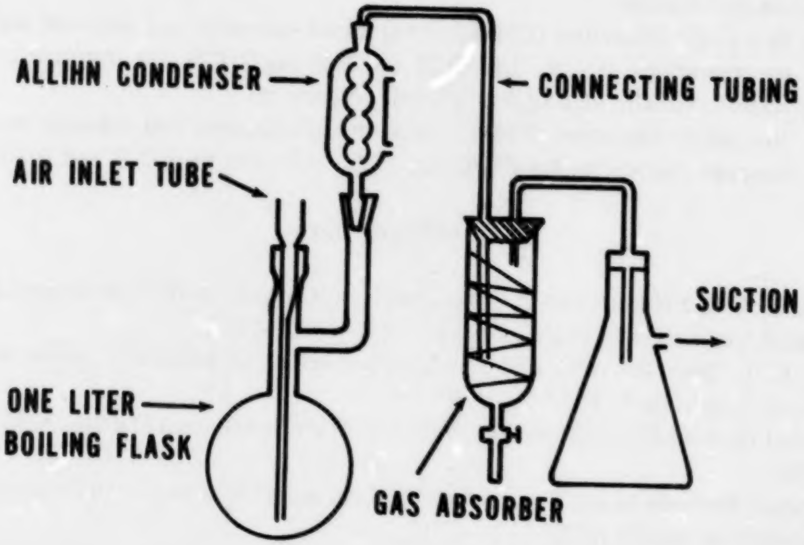

ALLIHN CONDENSER
CONNECTING TUBING
AIR INLET TUBE
SUCTION
ONE LITER
BOILING FLASK
GAS ABSORBER

FIGURE 1

CYANIDE DISTILLATION APPARATUS

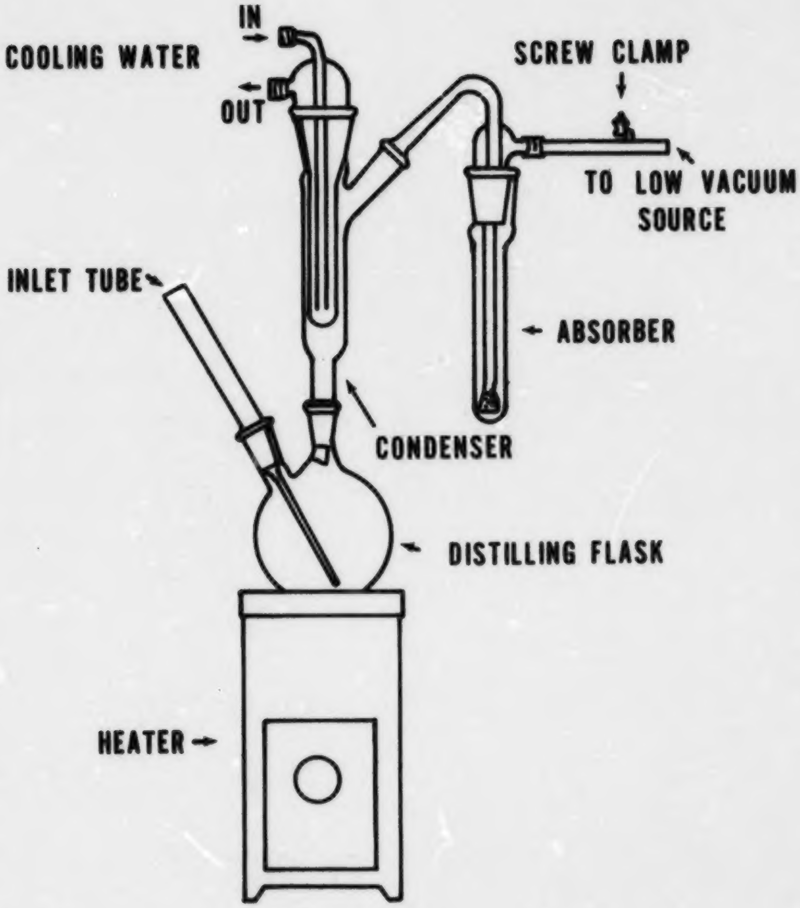
IN
COOLING WATER
OUT
SCREW CLAMP
TO LOW VACUUM SOURCE
INLET TUBE
ABSORBER
CONDENSER
DISTILLING FLASK
HEATER

FIGURE 2
CYANIDE DISTILLATION APPARATUS

CYANIDE, TOTAL

Method 335.3 (Colorimetric, Automated UV)

STORET NO. 00720

1. Scope and Application
   1.1 This method is applicable to the determination of cyanide in drinking and surface waters, domestic and industrial wastes.
   1.2 The applicable range is 5 to 500 ug/1.
2. Summary of Methods
   2.1 The cyanide as hydrocyanic acid (HCN), is released from cyanide complexes by means of UV digestion and distillation. Cyanides are converted to cyanogen chloride by reactions with chloramine-T which subsequently reacts with pyridine and barbituric acid to give a red-colored complex.
3. Sample Handling and Preservation
   3.1 The sample should be collected in plastic bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.
   3.2 Samples must be preserved with 2 m1 of 10 N sodium hydroxide per liter of sample (pH ≥ 12) at the time of collection.
   3.3 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.
   3.4 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.
4. Interferences
   4.1 Thiocyanates are a positive interference. During the UV digestion thiocyanates are decomposed to cyanide.
   4.2 Sulfides adversely affect the colorimetric procedure. If a drop of the sample on lead acetate test paper indicates the presence of sulfide, treat 25 m1 more of the stabilized sample (pH ≥ 12) than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of

cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

5. Apparatus

5.1 Technicon AutoAnalyzer
  5.1.1 Sampler
  5.1.2 Manifold with UV digestor
  5.1.3 Proportioning pump
  5.1.4 Heating bath with distillation coil
  5.1.5 Distillation head.
  5.1.6 Colorimeter equipped with a 15 mm flowcell and 570 nm filter.
  5.1.7 Recorder.

6. Reagents

6.1 Distillation reagent: Carefully add 250 ml of 85% phosphoric acid and 50 ml of hypophosphorus acid to 700 ml of distilled water, mix and dilute to one liter with distilled water.

6.2 Phosphate buffer, pH 5.2: Dissolve 13.6 g of potassium dihydrogen phosphate and 0.28 g of disodium phosphate in 900 ml of distilled water and dilute to one liter.

6.3 Chloramine-T: Dissolve 2.0 g of chloramine-T in 500 ml of distilled water.

6.4 Pyridine barbituric acid reagent: Place 15 g of barbituric acid in a one liter beaker. Wash the sides of the beaker with about 100 ml of distilled water. Add 75 ml of pyridine and mix. Add 15 ml of conc. HCl and mix. Dilute to about 900 ml with distilled water and mix until all the barbituric acid has dissolved. Transfer the solution to a one liter flask and dilute to the mark.

6.5 Sodium hydroxide, 1 N: Dissolve 40 g of NaOH in 500 ml of distilled water and dilute to one liter.

6.6 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 ml of distilled water and mix. Dilute to one liter. Standardize with 0.0192 N $AgNO_3$ to appropriate concentration. 1 ml = 1 mg CN.

6.7 All working standards should contain 2 ml of 1 N NaOH (6.5) per 100 ml.

7. Procedure

7.1 Set up the manifold as shown in Figure 1 in a hood or a well-ventilated area.

7.2 Set temperature of the heating bath at 150°C.

7.3 Allow colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line.

7.4 Place appropriate standards in the sampler in order of decreasing concentration. Complete loading of sampler tray with unknown samples.

7.5 When the baseline becomes steady begin the analyses.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of standards against concentration values. Compute concentrations of samples by comparing sample peak heights with standards.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

Bibliography

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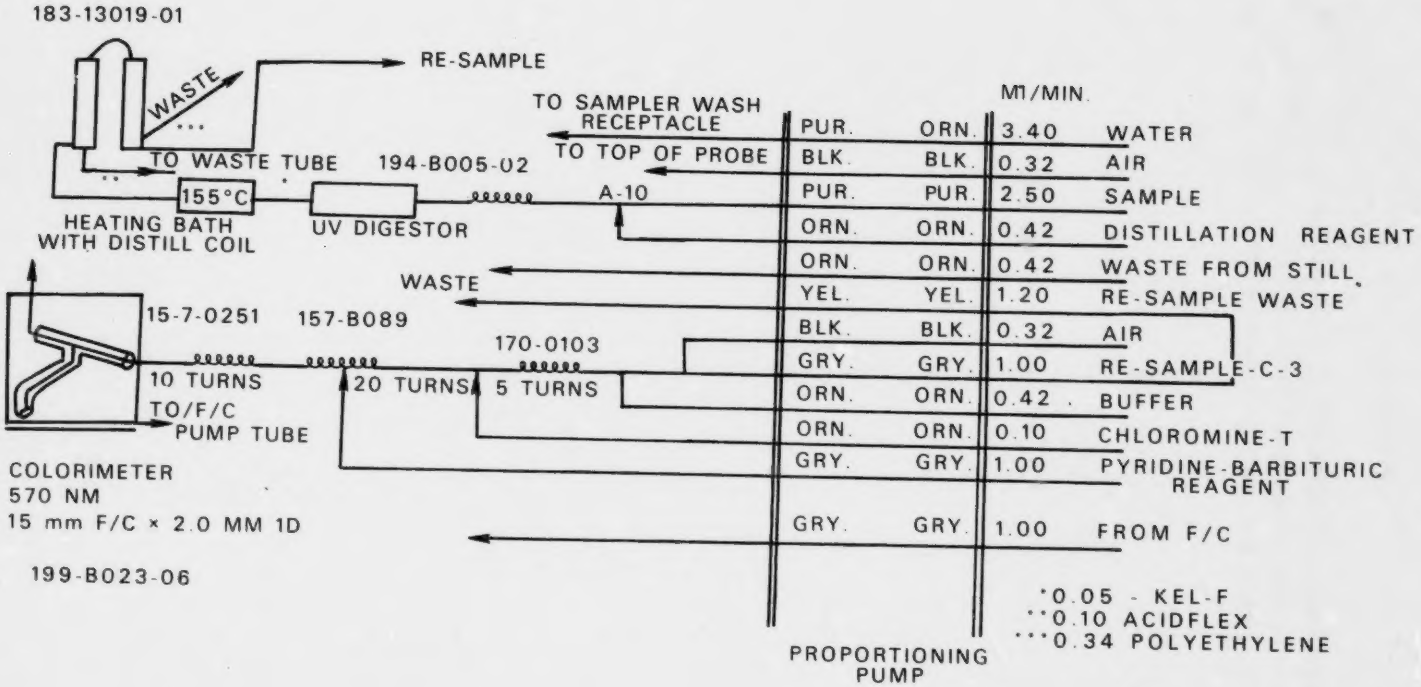
183-13019-01
RE-SAMPLE
WASTE
TO SAMPLER WASH RECEPTACLE
TO TOP OF PROBE
TO WASTE TUBE
194-B005-02
A-10
155°C
HEATING BATH WITH DISTILL COIL
UV DIGESTOR
WASTE
15-7-0251
157-B089
170-0103
10 TURNS
20 TURNS
5 TURNS
TO/F/C PUMP TUBE
COLORIMETER
570 NM
15 mm F/C × 2.0 MM 1D
199-B023-06
Ml/MIN.
PUR. ORN. 3.40 WATER
BLK. BLK. 0.32 AIR
PUR. PUR. 2.50 SAMPLE
ORN. ORN. 0.42 DISTILLATION REAGENT
ORN. ORN. 0.42 WASTE FROM STILL
YEL. YEL. 1.20 RE-SAMPLE WASTE
BLK. BLK. 0.32 AIR
GRY. GRY. 1.00 RE-SAMPLE-C-3
ORN. ORN. 0.42 BUFFER
ORN. ORN. 0.10 CHLOROMINE-T
GRY. GRY. 1.00 PYRIDINE-BARBITURIC REAGENT
GRY. GRY. 1.00 FROM F/C
*0.05 - KEL-F
**0.10 ACIDFLEX
***0.34 POLYETHYLENE
PROPORTIONING PUMP

FIGURE 1. CYANIDE MANIFOLD AA11

'AJ

FLUORIDE, TOTAL

Method 340.1 (Colorimetric, SPADNS with Bellack Distillation)

STORET NO. Total 00951
Dissolved 00950

1. Scope and Application
   1.1 This method is applicable to the measurement of fluoride in drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The method covers the range from 0.1 to about 1.4 mg/l F. This range may be extended to 1000 mg/l using the Fluoride Ion Selective Electrode Method (340.2) after distillation.
2. Summary of Method
   2.1 Following distillation to remove interferences, the sample is treated with the SPADNS reagent. The loss of color resulting from the reaction of fluoride with the zirconyl-SPADNS dye is a function of the fluoride concentration.
3. Comments
   3.1 The SPADNS reagent is more tolerant of interfering materials than other accepted fluoride reagents. Reference to Table 414:1, p 388, Standard Methods for the Examination of Waters and Wastewaters, 14th Edition, will help the analyst decide if distillation is required. The addition of the highly colored SPADNS reagent must be done with utmost accuracy because the fluoride concentration is measured as a difference of absorbance in the blank and the sample. A small error in reagent additon is the most prominent source of error in this test.
   3.2 Care must be taken to avoid overheating the flask above the level of the solution. This is done by maintaining an even flame entirely under the boiling flask.
4. Apparatus
   4.1 Distillation apparatus: A 1-liter round-bottom, long-necked pyrex boiling flask, connecting tube, efficient condenser, thermometer adapter and thermometer reading to 200°C. All connections should be ground glass. Any apparatus equivalent to that shown in Figure 1 is acceptable.
   4.2 Colorimeter: One of the following
      4.2.1 Spectrophotometer for use at 570 nm providing a light path of at least 1 cm.
      4.2.2 Filter photometer equipped with a greenish yellow filter having maximum transmittance at 550 to 580 nm and a light path of at least 1 cm.
5. Reagents
   5.1 Sulfuric acid, H_2SO_4, conc.

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5.2 Silver sulfate, Ag_2SO_4 crystals.

5.3 Stock fluoride solution: Dissolve 0.221 g anhydrous sodium fluoride, NaF, in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.1 mg F.

5.4 Standard fluoride solution: Place 100 ml stock fluoride solution (5.3) in a 1 liter volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.010 mg F.

5.5 SPADNS solution: Dissolve 0.958 g SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, in distilled water in a 500 ml volumetric flask and dilute to the mark. Stable indefinitely if protected from direct sunlight.

5.6 Zirconyl-acid reagent: Dissolve 0.133 g zirconyl chloride octahydrate, $Zr0Cl_2 \cdot 8H_2O$ in approximately 25 ml distilled water in a 500 ml volumetric flask. Add 350 ml conc HCl and dilute to the mark with distilled water.

5.7 Acid-zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution (5.5) and zirconyl-acid reagent (5.6). The combined reagent is stable for at least 2 years.

5.8 Reference solution: Add 10 ml SPADNS solution (5.5) to 100 ml distilled water. Dilute 7 ml conc HCl to 10 ml and add to the dilute SPADNS solution. This solution is used for zeroing the spectrophotometer or photometer. It is stable and may be used indefinitely.

5.9 Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water (CAUTION: Toxic-avoid ingestion).

6. Procedure

6.1 Preliminary distillation

6.1.1 Place 400 ml distilled water in the distilling flask.

6.1.2 Carefully add 200 ml conc. H_2SO_4 and swirl until contents are homogeneous.

6.1.3 Add 25 to 35 glass beads, connect the apparatus (Figure 1) making sure all joints are tight.

6.1.4 Heat slowly at first, then as rapidly as the efficiency of the condenser will permit (distillate must be cool) until the temperature of the flask contents reaches exactly 180°C. Discard the distillate. This process removes fluoride contamination and adjusts the acid-water ratio for subsequent distillations.

6.1.5 Cool to 120°C or below.

6.1.6 Add 300 ml sample, mix thoroughly, distill as in 6.1.4 until temperature reaches 180°C. Do not heat above 180°C to prevent sulfate carryover.

6.1.7 Add Ag_2SO_4 (5.2) at a rate of 5 mg/mg Cl when high chloride samples are distilled.

6.1.8 Use the sulfuric acid solution in the flask repeatedly until the contaminants from the samples accumulate to such an extent that recovery is affected or interferences appear in the distillate. Check periodically by distilling standard fluoride samples.

6.1.9 High fluoride samples may require that the still be flushed by using distilled water and combining distillates.

6.2 Colorimetric Determination:

6.2.1 Prepare fluoride standards in the range 0 to 1.40 mg/1 by diluting appropriate quantities of standard fluoride solution (5.4) to 50 ml with distilled water.

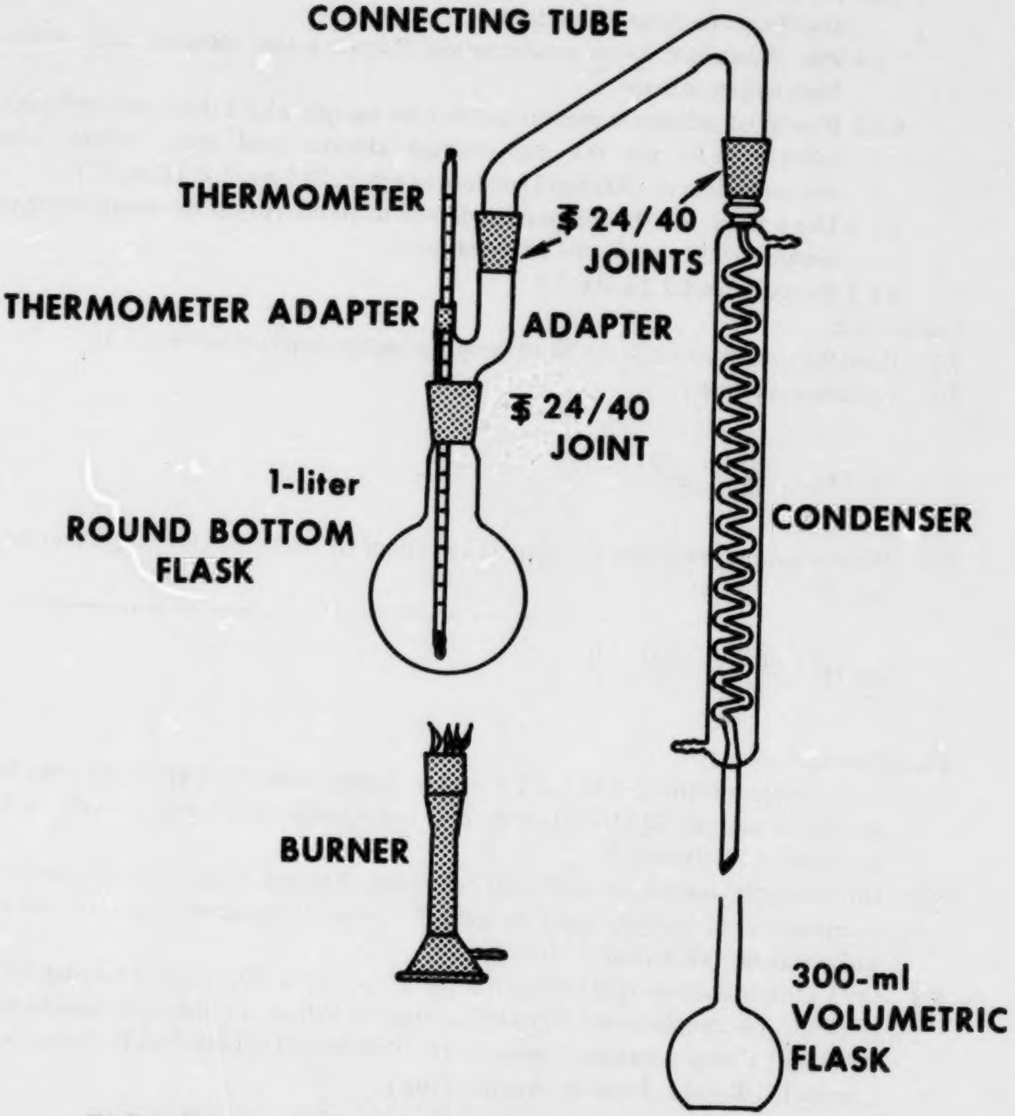
CONNECTING TUBE
THERMOMETER
₷ 24/40
JOINTS
THERMOMETER ADAPTER
ADAPTER
₷ 24/40
JOINT
1-liter
ROUND BOTTOM
FLASK
CONDENSER
BURNER
300-ml
VOLUMETRIC
FLASK

FIGURE 1 DIRECT DISTILLATION APPARATUS FOR FLUORIDE.

6.2.2 Pipet 5.00 ml each of SPADNS solution (5.5) and zirconyl-acid reagent (5.6) or 10.00 ml of the mixed acid-zirconyl-SPADNS reagent (5.7) to each standard and mix well.

6.2.3 Set photometer to zero with reference solution (5.8) and immediately obtain absorbance readings of standards.

6.2.4 Plot absorbance versus concentration. Prepare a new standard curve whenever fresh reagent is made.

6.2.5 If residual chlorine is present pretreat the sample with 1 drop (0.05 ml) $NaAsO_2$ solution (5.9) per 0.1 mg residual chlorine and mix. Sodium arsenite concentrations of 1300 mg/1 produce an error of 0.1 mg/1 at 1.0 mg/1 F.

6.2.6 Use a 50 ml sample or a portion diluted to 50 ml. Adjust the temperature of the sample to that used for the standard curve.

6.2.7 Perform step 6.2.2 and 6.2.3.

7. Calculations

7.1 Read the concentration in the 50 ml sample using the standard curve (6.2.4)

7.2 Calculate as follows:

$$\text{mg/l F} = \frac{\text{mgF} \times 1{,}000}{\text{ml sample}}$$

7.3 When a sample (ml sample) is diluted to a volume (B) and then a portion (C) is analyzed, use:

$$\text{mg/l F} = \frac{\text{mgF} \times 1{,}000}{\text{ml sample}} \times \frac{B}{C}$$

8. Precision and Accuracy

8.1 On a sample containing 0.83 mg/1 F with no interferences, 53 analysts using the Bellack distillation and the SPADNS reagent obtained a mean of 0.81 mg/1 F with a standard deviation of ±0.089 mg/1.

8.2 On a sample containing 0.57 mg/1 F (with 200 mg/1 SO_4 and 10 mg/1 Al as interferences) 53 analysts using the Bellack distillation obtained a mean of 0.60 mg/1F with a standard deviation of ±0.103 mg/1.

8.3 On a sample containing 0.68 mg/1 F (with 200 mg/1 SO_4, 2 mg/1 Al and 2.5 mg/1 $[Na(PO_3)_6]$ as interferences), 53 analysts using the Bellack distillation obtained a mean of 0.72 mg/1 F with a standard deviation of ±0.092 mg/1. (Analytical Reference Service, Sample 111-B water, Fluoride, August, 1961.)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, p. 389–390 (Method No. 414A, Preliminary Distillation Step) and p. 393–394 (Method 414C SPADNS) 14th Edition, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1179–72, Method A, p. 310 (1976).

FLUORIDE

Method 340.2 (Potentiometric, Ion Selective Electrode)

STORET NO: Total 00951
Dissolved 00950

1. Scope and Application
   - 1.1 This method is applicable to the measurement of fluoride in drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 Concentration of fluoride from 0.1 up to 1000 mg/liter may be measured.
   - 1.3 For Total or Total Dissolved Fluoride, the Bellack distillation is required for NPDES monitoring but is not required for SDWA monitoring.
2. Summary of Method
   - 2.1 The fluoride is determined potentiometrically using a fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale or a selective ion meter having a direct concentration scale for fluoride.
   - 2.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/Ag Cl, Cl^-(0.3), F^-(0.001) LaF/test solution/SCE/.
3. Interferences
   - 3.1 Extremes of pH interfere; sample pH should be between 5 and 9. Polyvalent cations of Si^{+4}, Fe^{+3} and Al^{+3} interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer (described below) containing a strong chelating agent preferentially complexes aluminum (the most common interference), silicon and iron and eliminates the pH problem.
4. Sampling Handling and Preservation
   - 4.1 No special requirements.
5. Apparatus
   - 5.1 Electrometer (pH meter), with expanded mv scale, or a selective ion meter such as the Orion 400 Series.
   - 5.2 Fluoride Ion Activity Electrode, such as Orion No. 94–09(1).
   - 5.3 Reference electrode, single junction, sleeve-type, such as Orion No. 90–01, Beckman No. 40454, or Corning No. 476010.
   - 5.4 Magnetic Mixer, Teflon-coated stirring bar.

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6. Reagents

6.1 Buffer solution, pH 5.0–5.5: To approximately 500 ml of distilled water in a 1 liter beaker add 57 ml of glacial acetic acid, 58 g of sodium chloride and 4 g of CDTA(2). Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer solution to a 1 liter volumetric flask and dilute to the mark with distilled water. For work with brines, additional NaCl should be added to raise the chloride level to twice the highest expected level of chloride in the sample.

6.2 Sodium fluoride, stock solution: 1.0 ml = 0.1 mg F. Dissolve 0.2210 g of sodium fluoride in distilled water and dilute to 1 liter in a volumetric flask. Store in chemical-resistant glass or polyethylene.

6.3 Sodium fluoride, standard solution: 1.0 ml = 0.01 mg F. Dilute 100.0 ml of sodium fluoride stock solution (6.2) to 1000 ml with distilled water.

6.4 Sodium hydroxide, 5N: Dissolve 200 g sodium hydroxide in distilled water, cool and dilute to 1 liter.

7. Calibration

7.1 Prepare a series of standards using the fluoride standard solution (6.3) in the range of 0 to 2.00 mg/1 by diluting appropriate volumes to 50.0 ml. The following series may be used:

Millimeters of Standard (1.0 ml = 0.01 mg/F)	Concentration when Diluted to 50 ml, mg F/liter
0.00	0.00
1.00	0.20
2.00	0.40
3.00	0.60
4.00	0.80
5.00	1.00
6.00	1.20
8.00	1.60
10.00	2.00

7.2 Calibration of Electrometer: Proceed as described in (8.1). Using semilogarithmic graph paper, plot the concentration of fluoride in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale. Calibration of a selective ion meter: Follow the directions of the manufacturer for the operation of the instrument.

8. Procedure

8.1 Place 50.0 ml of sample or standard solution and 50.0 ml of buffer (See Note) in a 150 ml beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 mg/liter F, it may require as long as five minutes to reach a stable meter reading; high concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown using the standard curve. If a selective ion meter is used, read the fluoride level in the unknown sample directly in mg/1 on the fluoride scale.

NOTE: For industrial waste samples, this amount of buffer may not be adequate. Analyst should check pH first. If highly basic (> 9), add 1 N HCl to adjust pH to 8.3.

9. Precision and Accuracy

9.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 0.85 mg/1 fluoride and no interferences was analyzed by 111 analysts; a mean of 0.84 mg/1 with a standard deviation of ±0.03 was obtained.

9.2 On the same study, a synthetic sample containing 0.75 mg/1 fluoride, 2.5 mg/1 polyphosphate and 300 mg/1 alkalinity, was analyzed by the same 111 analysts; a mean of 0.75 mg/1 fluoride with a standard deviation of ±0.036 was obtained.

Bibliography

1. Patent No. 3,431,182 (March 4, 1969).
2. CDTA is the abbreviated designation of 1,2-cyclohexylene dinitrilo tetraacetic acid. (The monohydrate form may also be used.) Eastman Kodak 15411, Mallinckrodt 2357, Sigma D 1383, Tridom-Fluka 32869-32870 or equivalent.
3. Standard Methods for the Examination of Water and Wastewaters, p 389, Method No. 414A, Preliminary Distillation Step (Bellack), and p 391, Method No. 414B, Electrode Method, 14th Edition (1975).
4. Annual Book of ASTM Standards, Part 31, "Water", Standard D1179–72, Method B, p 312 (1976).

FLUORIDE

Method 340.3 (Colorimetric, Automated Complexone)

STORET NO. Total 00951
Dissolved 00950

1. Scope and Application
    - 1.1 This method is applicable to drinking, surface and saline waters, domestic and industrial wastes. The applicable range of the method is 0.05 to 1.5 mg F/1. Twelve samples per hour can be analyzed.
    - 1.2 For Total or Total Dissolved Fluoride, the Bellack Distillation must be performed on the samples prior to analysis by the complexone method.
2. Summary of Method
    - 2.1 Fluoride ion reacts with the red cerous chelate of alizarin complexone. It is unlike other fluoride procedures in that a positive color is developed as contrasted to a bleaching action in previous methods.
3. Sample Handling and Preservation
    - 3.1 No special requirements.
4. Interferences
    - 4.1 Method is free from most anionic and cationic interferences, except aluminum, which forms an extremely stable fluoro compound, AlF_6^{-3}. This is overcome by treatment with 8-hydroxyquinoline to complex the aluminum and by subsequent extraction with chloroform. At aluminum levels below 0.2 mg/1, the extraction procedure is not required.
5. Apparatus
    - 5.1 Technicon AutoAnalyzer Unit consisting of:
        - 5.1.1 Sampler I.
        - 5.1.2 Manifold.
        - 5.1.3 Proportioning pump.
        - 5.1.4 Continuous filter.
        - 5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 650 nm filters.
        - 5.1.6 Recorder equipped with range expander.
6. Reagents
    - 6.1 Sodium acetate solution: Dissolve 272 g (2 moles) of sodium acetate in distilled water and dilute to 1 liter.
    - 6.2 Acetic acid-8-hydroxyquinoline solution: Dissolve 6 g of 8-hydroxyquinoline in 34 ml of conc. acetic acid, and dilute to 1 liter with distilled water.

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6.3 Chloroform: Analytical reagent grade.

6.4 Ammonium acetate solution (6.7%): Dissolve 67 g of ammonium acetate in distilled water and dilute to 1 liter.

6.5 Hydrochloric acid (2 N): Dilute 172 ml of conc. HCl to 1 liter.

6.6 Lanthanum alizarin fluoride blue solution(1): Dissolve 0.18 g of alizarin fluoride blue in a solution containing 0.5 ml of conc. ammonium hydroxide and 15 ml of 6.7% ammonium acetate (6.4). Add a solution that contains 41 g of anhydrous sodium carbonate and 70 ml of glacial acetic acid in 300 ml of distilled water. Add 250 ml of acetone. Dissolve 0.2 g of lanthanum oxide in 12.5 ml of 2 N hydrochloric acid (6.5) and mix with above solution. Dilute to 1 liter.

6.7 Stock solution: Dissolve 2.210 g of sodium fluoride in 100 ml of distilled water and dilute to 1 liter in a volumetric flask. 1.0 ml = 1.0 mg F.

6.8 Standard Solution: Dilute 10.0 ml of stock solution to 1 liter in a volumetric flask. 1.0 ml = 0.01 mg F.

6.8.1 Using standard solution, prepare the following standards in 100 ml volumetric flask:

mg F/l	ml Standard Solution/100 ml
0.05	0.5
0.10	1.0
0.20	2.0
0.40	4.0
0.60	6.0
0.80	8.0
1.00	10.0
1.20	12.0
1.50	15.0

7. Procedure

7.1 Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.5 minutes.

7.4 Arrange fluoride standards in Sampler in order of decreasing concentration. Complete loading of Sampler tray with unknown samples.

7.5 Switch sample line from distilled water to Sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed fluoride standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

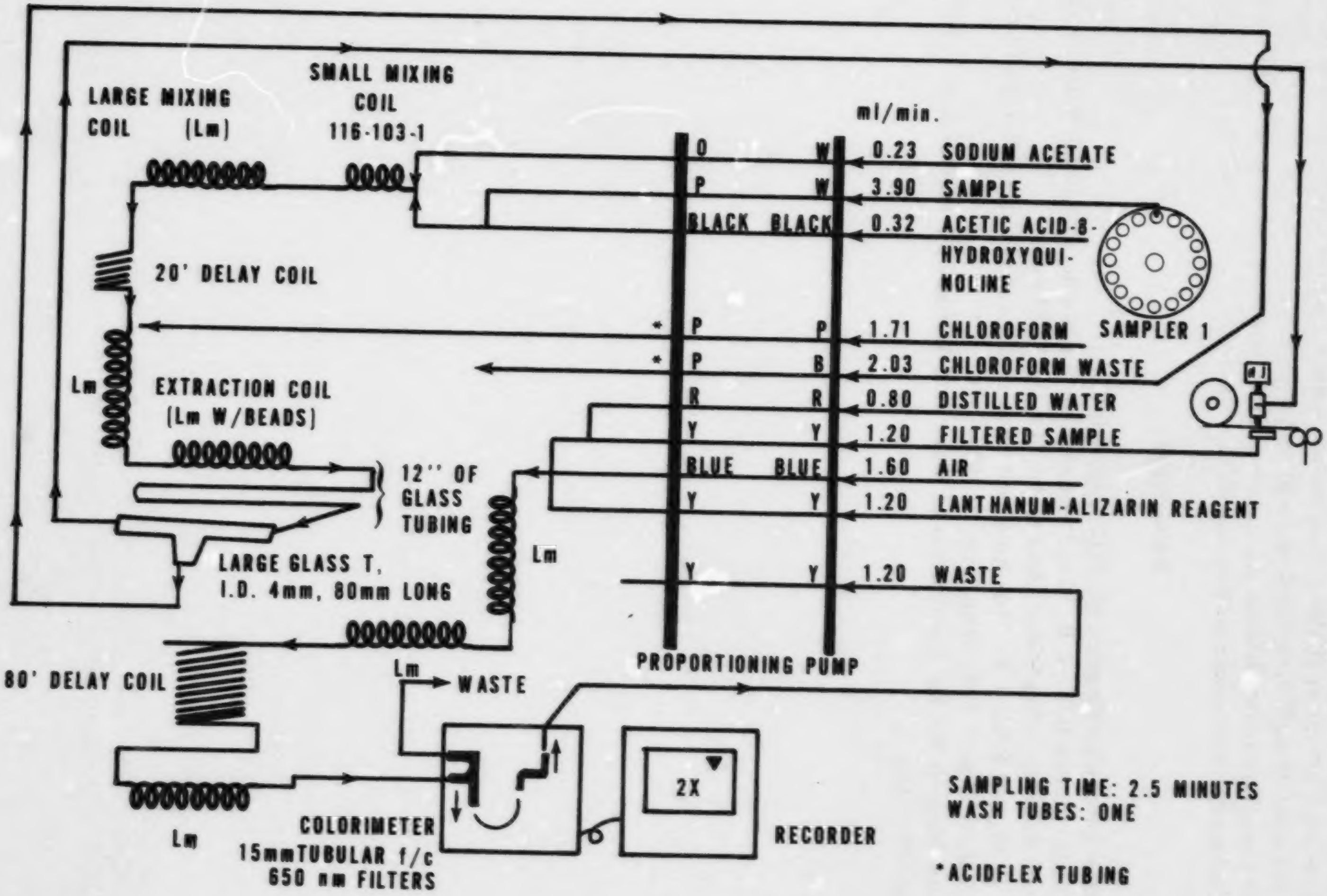
9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 0.06, 0.15, and 1.08 mg F/1, the standard deviation was ±0.018.

9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.14 and 1.25 mg F/1, recoveries were 89% and 102%, respectively.

Bibliography

1. J. T. Baker Laboratory Chemical No. J112 or equivalent.
2. Greenhaigh, R., and Riley, J. P., "The Determination of Fluorides in Natural Waters, with Particular Reference to Sea Water". Anal. Chim. Acta, 25, 179 (1961).
3. Chan, K. M., and Riley, J. P., "The Automatic Determination of Fluoride in Sea Water and Other Natural Water". Anal. Chim. Acta, 35, 365 (1966).
4. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 614, Method 603, (1975).


LARGE MIXING COIL (Lm)
SMALL MIXING COIL 116-103-1
ml/min.
O
W
0.23
SODIUM ACETATE
P
W
3.90
SAMPLE
BLACK
BLACK
0.32
ACETIC ACID-8-HYDROXYQUINOLINE
20' DELAY COIL
*
P
P
1.71
CHLOROFORM
SAMPLER 1
*
P
B
2.03
CHLOROFORM WASTE
Lm
EXTRACTION COIL (Lm W/BEADS)
R
R
0.80
DISTILLED WATER
Y
Y
1.20
FILTERED SAMPLE
BLUE
BLUE
1.60
AIR
12'' OF GLASS TUBING
Y
Y
1.20
LANTHANUM-ALIZARIN REAGENT
Lm
LARGE GLASS T, I.D. 4mm, 80mm LONG
Y
Y
1.20
WASTE
PROPORTIONING PUMP
80' DELAY COIL
Lm
WASTE
2X
Lm
COLORIMETER 15mmTUBULAR f/c 650 nm FILTERS
RECORDER

SAMPLING TIME: 2.5 MINUTES
WASH TUBES: ONE

*ACIDFLEX TUBING

FIGURE 1. FLUORIDE MANIFOLD AA-I

IODIDE

Method 345.1 (Titrimetric)

STORET NO. 71865

1. Scope and Application
   1.1 This method is applicable to drinking, surface and saline waters, sewage and industrial waste effluents.
   1.2 The concentration range for this method is 2–20 mg/1 of iodide.
2. Summary of Method
   2.1 After pretreatment to remove interferences, the sample is analyzed for iodide by converting the iodide to iodate with bromine water and titrating with phenylarsine oxide (PAO) or sodium thiosulfate.
3. Sample Handling and Preservation
   3.1 Store at 4°C and analyze as soon as possible.
4. Interferences
   4.1 Iron, manganese and organic matter can interfere; however, the calcium oxide pretreatment removes or reduces these to insignificant concentrations.
   4.2 Color interferes with the observation of indicator and bromine-water color changes. This interference is eliminated by the use of a pH meter instead of a pH indicator and the use of standardized amounts of bromine water and sodium formate solution instead of observing the light yellow color changes.
5. Reagents
   5.1 Acetic Acid Solution (1:8): Mix 100 ml of glacial acetic acid with 800 ml of distilled water.
   5.2 Bromine Water: In a fume hood, add 0.2 ml bromine to 500 ml distilled water. Stir with a magnetic stirrer and a Teflon-coated stirring bar for several hours or until the bromine dissolves. Store in a glass-stoppered colored bottle.
   5.3 Calcium Oxide (CaO): Anhydrous, powdered.
   5.4 Potassium Iodide (KI): Crystals, ACS Reagent Grade.
   5.5 Sodium Acetate Solution (275 g/1): Dissolve 275 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in distilled water. Dilute to 1 liter and filter.
   5.6 Sodium Formate Solution (500 g/1): Dissolve 50 g of sodium formate ($NaCHO_2$) in hot distilled water and dilute to 100 ml.
   5.7 Nitrogen Gas: Cylinder.
   5.8 Sulfuric Acid Solution (1:4): Slowly add 200 ml of H_2SO_4 (sp. gr. 1.84) to 800 ml of distilled water.
   5.9 Phenylarsine Oxide (0.0375 N): Hach Chemical Co. or equivalent. Standardize with 0.0375 N potassium biiodate (5.15, 5.18).

Issued 1974

5.10 Phenylarsine Oxide Working Standard (0.0075 N): Transfer 100 ml of commercially available 0.0375 N phenylarsine oxide (5.9) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.11 Commercially available starch indicators such as thyodene or equivalent may be used.

5.12 Sodium Thiosulfate, Stock Solution, 0.75 N: Dissolve 186.15 g ($Na_2S_2O_3 \cdot 5H_2O$) in boiled and cooled distilled water and dilute to 1.0 liter. Preserve by adding 5 ml chloroform.

5.13 Sodium Thiosulfate Standard Titrant, 0.0375 N: Prepare by diluting 50.0 ml of stock solution to 1.0 liter. Preserve by adding 5 ml of chloroform. Standardize with 0.0375 N potassium biiodate (5.15, 5.18).

5.14 Sodium Thiosulfate Working Standard (0.0075 N): Transfer 100 ml of sodium thiosulfate standard titrant (5.13) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.15 Potassium Biiodate Standard, 0.0375 N: Dissolve 4.873 g potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liter. Dilute 250 ml to 1.0 liter for 0.0375 N biiodate solution.

5.16 Starch Solution: Prepare an emulsion of 10 g of soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator. Commercially available, powdered starch indicators may be used in place of starch solution.

5.17 Potassium Fluoride ($KF \cdot 2H_2O$): ACS Reagent Grade

5.18 Standardization of 0.0375 N Phenylarsine Oxide and 0.0375 N sodium thiosulfate: Dissolve approximately 2 g (± 1.0 g) KI (5.4) in 100 to 150 ml distilled water; add 10 ml H_2SO_4 solution (5.8) followed by 20 ml standard potassium biiodate solution (5.15). Place in dark for 5 minutes, dilute to 300 ml and titrate with phenylarsine oxide (5.9) or sodium thiosulfate standard titrant (5.13) to a pale straw color. Add a small scoop of indicator (5.11). Wait until homogeneous color develops and continue the titration drop by drop until the blue color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

6. Procedure

6.1 Pretreatment

6.1.1 Add a visible excess of CaO (5.3) to 400 ml of sample. Stir or shake vigorously for approximately 5 minutes. Filter through a dry, moderately retentive filter paper, discarding the first 75 ml.

6.2 Iodide Determination

6.2.1 Place 100 ml of pretreated sample (6.1) or a fraction thereof diluted to that volume, into a 150 ml beaker. Add a Teflon-coated stirring bar and place on a magnetic stirrer. Insert a pH electrode and adjust the pH to approximately 7 or slightly less by the dropwise addition of H_2SO_4 solution (5.8).

6.2.2 Transfer the sample to a 250 ml wide-mouthed conical flask. Wash beaker with small amounts of distilled water and add washings to the flask.

NOTE: A 250 ml iodine flask would increase accuracy and precision by preventing possible loss of the iodine generated upon addition of potassium iodide and sulfuric acid (6.3.1).

6.2.3 Add 15 ml sodium acetate solution (5.5) and 5 ml acetic acid solution (5.1). Mix well. Add 40 ml bromine water solution (5.2); mix well. Wait 5 minutes.

6.2.4 Add 2 ml sodium formate solution (5.6); mix well. Wait 5 minutes.

6.2.5 Purge the space above the sample with a gentle stream of nitrogen (5.7) for approximately 30 seconds to remove bromine fumes.

6.2.6 If a precipitate forms (iron), add 0.5 g $KF \cdot 2H_2O$ (5.17).

6.2.7 A distilled water blank must be run with each set of samples because of iodide in reagents. If a blank is consistently shown to be zero for a particular "lot" of chemicals it can then be ignored.

6.3 Titration

6.3.1 Dissolve approximately 1 g potassium iodide (5.4) in sample. Add 10 ml of H_2SO_4 solution (5.8) and place in dark for 5 minutes.

6.3.2 Titrate with phenylarsine oxide working standard (5.10) or sodium thiosulfate working standard solution (5.14) adding indicator (5.11 or 5.15) as end point is approached (light straw color). Titrate to colorless solution. Disregard returning blue color.

7. Calculations

$$I^{-}(\text{mg/l}) = 21{,}150 \left(\frac{\text{ml} \times N}{V}\right)$$

where:

ml = the number of ml of PAO needed to titrate the sample.
N = the normality of the PAO used to titrate the sample.
V = the volume of sample taken (100 ml or a fraction thereof)
21,150 was calculated from the number of equivalents of iodine produced when the potassium iodide was added and from the rearrangement of the equation to produce the value in terms of mg/1.

8. Precision and Accuracy

8.1 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent, at concentrations of 1.6, 4.1, 6.6, 11.6 and 21.6 mg/1 of iodide, the standard deviations were ±0.23, ±0.17, ±0.10, ±0.06 and ±0.50 mg/1, respectively.

8.2 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent at concentrations of 4.1, 6.6, 11.6 and 21.6 mg/1 of iodide, recoveries were 80, 97, 97 and 92%, respectively.

Bibliography

1. Annual Book of ASTM Standards, Part 31",Water", Standard D1246–68, p 328, Method C (1976)
2. Bender, D. F., "Modification of the Iodimetric Titration Method for the Determination of Bromide and its Application to Mixed Domestic-Industrial Waste Effluent", Analyst (London) 100, p400–404 (June 1975).

NITROGEN, AMMONIA

Method 350.1 (Colorimetric, Automated Phenate)

STORET NO. Total 00610
Dissolved 00608

1. Scope and Application
   1.1 This method covers the determination of ammonia in drinking, surface, and saline waters, domestic and industrial wastes in the range of 0.01 to 2.0 mg/1 NH_3 as N. This range is for photometric measurements made at 630–660 nm in a 15 mm or 50 mm tubular flow cell. Higher concentrations can be determined by sample dilution. Approximately 20 to 60 samples per hour can be analyzed.
2. Summary of Method
   2.1 Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside.
3. Sample Handling and Preservation
   3.1 Preservation by addition of 2 ml conc. H_2SO_4 per liter and refrigeration at 4°C.
4. Interferences
   4.1 Calcium and magnesium ions may be present in concentration sufficient to cause precipitation problems during analysis. A 5% EDTA solution is used to prevent the precipitation of calcium and magnesium ions from river water and industrial waste. For sea water a sodium potassium tartrate solution is used.
   4.2 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. Sample color that absorbs in the photometric range used will also interfere.
5. Apparatus
   5.1 Technicon AutoAnalyzer Unit (AAI or AAII) consisting of:
      5.1.1 Sampler.
      5.1.2 Manifold (AAI) or Analytical Cartridge (AAII).
      5.1.3 Proportioning pump.
      5.1.4 Heating bath with double delay coil (AAI).
      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 630–660 nm filters.
      5.1.6 Recorder.
      5.1.7 Digital printer for AAII (optional).

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6. Reagents

6.1 Distilled water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer.

NOTE 1: All solutions must be made using ammonia-free water.

6.2 Sulfuric acid 5N: Air scrubber solution. Carefully add 139 ml of conc. sulfuric acid to approximately 500 ml of ammonia-free distilled water. Cool to room temperature and dilute to 1 liter with ammonia-free distilled water.

6.3 Sodium phenolate: Using a 1 liter Erlenmeyer flask, dissolve 83 g phenol in 500 ml of distilled water. In small increments, cautiously add with agitation, 32 g of NaOH. Periodically cool flask under water faucet. When cool, dilute to 1 liter with distilled water.

6.4 Sodium hypochlorite solution: Dilute 250 ml of a bleach solution containing 5.25% NaOCl (such as "Clorox") to 500 ml with distilled water. Available chlorine level should approximate 2 to 3%. Since "Clorox" is a proprietary product, its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Due to the instability of this product, storage over an extended period should be avoided.

6.5 Disodium ethylenediamine-tetraacetate (EDTA) (5%): Dissolve 50 g of EDTA (disodium salt) and approximately six pellets of NaOH in 1 liter of distilled water.

NOTE 2: On salt water samples where EDTA solution does not prevent precipitation of cations, sodium potassium tartrate solution may be used to advantage. It is prepared as follows:

6.5.1 Sodium potassium tartrate solution: 10% $NaKC_4H_4O_6 \cdot 4H_2O$. To 900 ml of distilled water add 100 g sodium potassium tartrate. Add 2 pellets of NaOH and a few boiling chips, boil gently for 45 minutes. Cover, cool, and dilute to 1 liter with ammonia-free distilled water. Adjust pH to 5.2 ±.05 with H_2SO_4. After allowing to settle overnight in a cool place, filter to remove precipitate. Then add 1/2 ml Brij-35(4) (available from Technicon Corporation) solution and store in stoppered bottle.

6.6 Sodium nitroprusside (0.05%): Dissolve 0.5 g of sodium nitroprusside in 1 liter of distilled water.

6.7 Stock solution: Dissolve 3.819 g of anhydrous ammonium chloride, NH_4Cl, dried at 105°C, in distilled water, and dilute to 1000 ml. 1.0 ml = 1.0 mg NH_3–N.

6.8 Standard Solution A: Dilute 10.0 ml of stock solution (6.7) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NH_3–N.

6.9 Standard solution B: Dilute 10.0 ml of standard solution A (6.8) to 100.0 ml with distilled water. 1.0 ml = 0.001 mg NH_3–N.

6.10 Using standard solutions A and B, prepare the following standards in 100 ml volumetric flasks (prepare fresh daily):

NH_3–N, mg/l	ml Standard Solution/100 ml
	Solution B
0.01	1.0
0.02	2.0
0.05	5.0
0.10	10.0
	Solution A
0.20	2.0
0.50	5.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

NOTE 3: When saline water samples are analyzed, Substitute Ocean Water (SOW) should be used for preparing the above standards used for the calibration curve; otherwise, distilled water is used. If SOW is used, subtract its blank background response from the standards before preparing the standard curve.

Substitute Ocean Water (SOW)

NaCl	24.53 g/l	$NaHCO_3$	0.20 g/l
$MgCl_2$	5.20 g/l	KBr	0.10 g/l
Na_2SO_4	4.09 g/l	H_3BO_3	0.03 g/l
$CaCl_2$	1.16 g/l	$SrCl_2$	0.03 g/l
KCl	0.70 g/l	NaF	0.003 g/l

7. Procedure

7.1 Since the intensity of the color used to quantify the concentration is pH dependent, the acid concentration of the wash water and the standard ammonia solutions should approximate that of the samples. For example, if the samples have been preserved with 2 ml conc. H_2SO_4/liter, the wash water and standards should also contain 2 ml conc. H_2SO_4/liter.

7.2 For a working range of 0.01 to 2.00 mg NH_3–N/1 (AAI), set up the manifold as shown in Figure 1. For a working range of .01 to 1.0 mg NH_3–N/1 (AAII), set up the manifold as shown in Figure 2. Higher concentrations may be accommodated by sample dilution.

7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through sample line.

7.4 For the AAI system, sample at a rate of 20/hr, 1:1. For the AAII use a 60/hr 6:1 cam with a common wash.

7.5 Arrange ammonia standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.6 Switch sample line from distilled water to sampler and begin analysis.

8. Calculations

8.1 Prepare appropriate standard curve derived from processing ammonia standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1.41, 0.77, 0.59 and 0.43 mg NH_3–N/1, the standard deviation was ±0.005.

9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.16 and 1.44 mg NH_3–N/1, recoveries were 107% and 99%, respectively.

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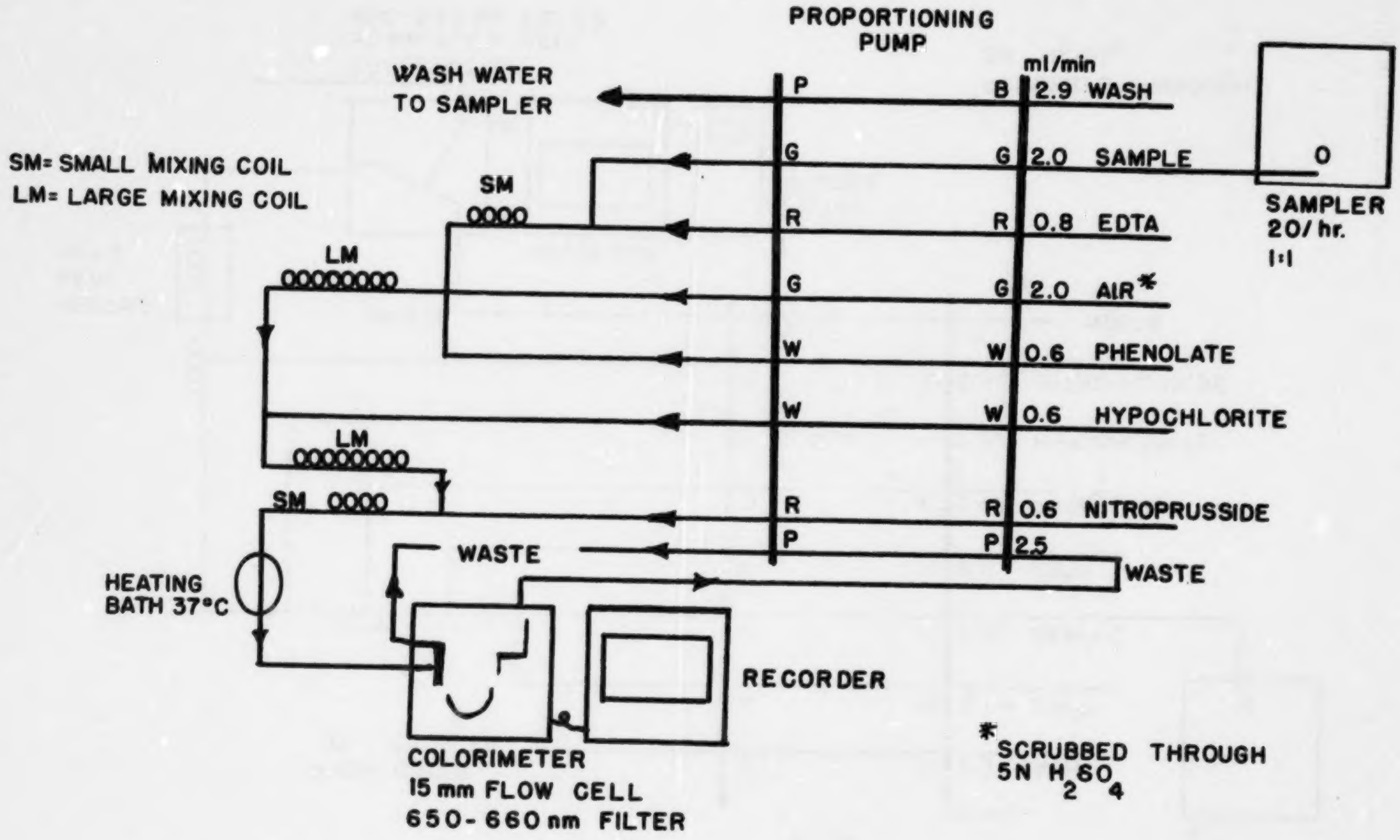
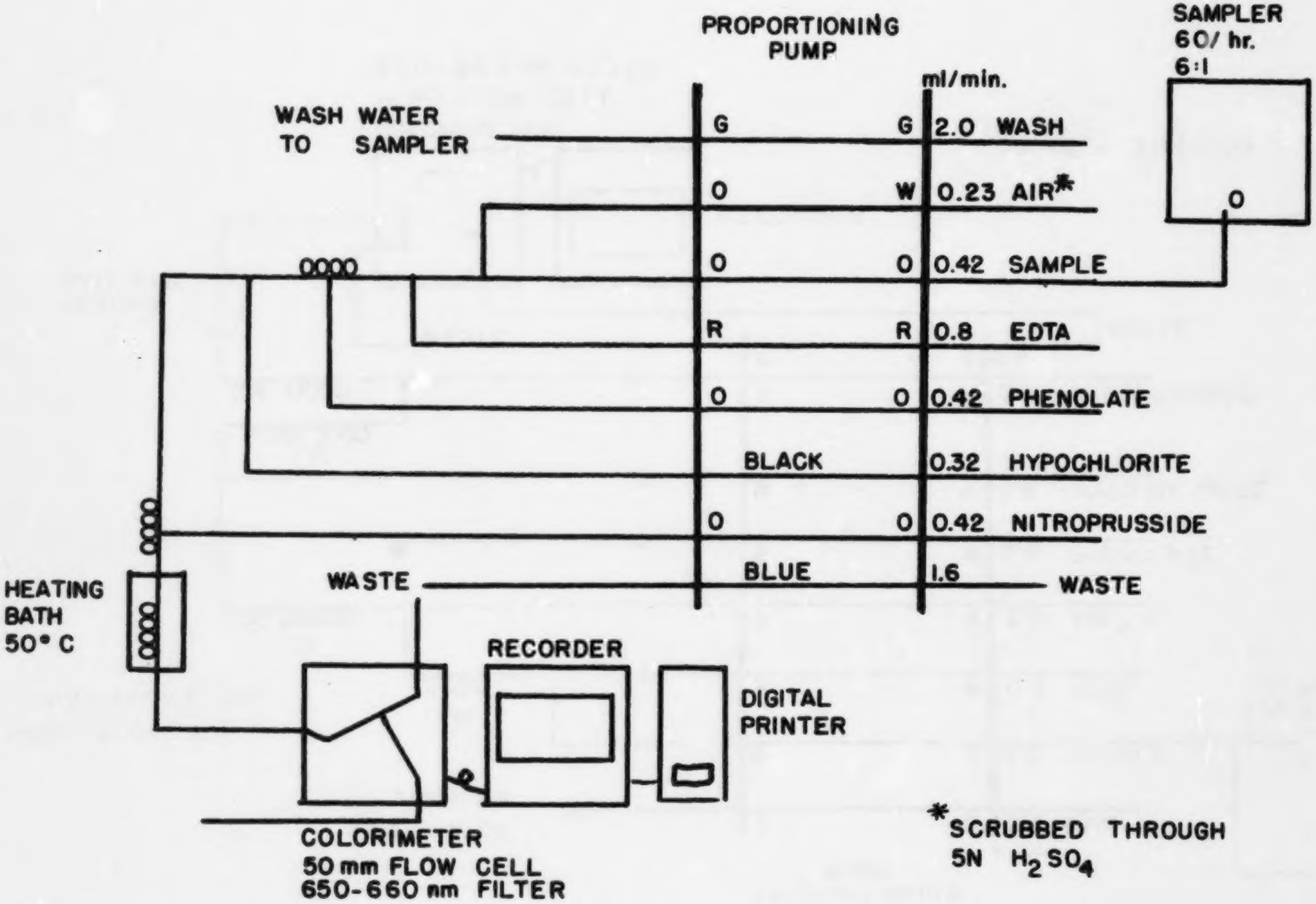

PROPORTIONING
PUMP
ml/min
WASH WATER
TO SAMPLER
SM= SMALL MIXING COIL
LM= LARGE MIXING COIL
SM
LM
LM
SM
P
G
R
G
W
W
R
P
B 2.9 WASH
G 2.0 SAMPLE
R 0.8 EDTA
G 2.0 AIR*
W 0.6 PHENOLATE
W 0.6 HYPOCHLORITE
R 0.6 NITROPRUSSIDE
P 2.5
WASTE
WASTE
SAMPLER
20/hr.
1:1
HEATING
BATH 37°C
RECORDER
COLORIMETER
15 mm FLOW CELL
650-660 nm FILTER
*SCRUBBED THROUGH
5N H2SO4

FIGURE 1 AMMONIA MANIFOLD AA I


PROPORTIONING PUMP
ml/min.
SAMPLER
60/ hr.
6:1
WASH WATER TO SAMPLER
G
G
2.0 WASH
O
W
0.23 AIR*
O
O
0.42 SAMPLE
R
R
0.8 EDTA
O
O
0.42 PHENOLATE
BLACK
0.32 HYPOCHLORITE
O
O
0.42 NITROPRUSSIDE
WASTE
BLUE
1.6
WASTE
HEATING BATH 50° C
RECORDER
DIGITAL PRINTER
COLORIMETER
50 mm FLOW CELL
650-660 nm FILTER

*SCRUBBED THROUGH 5N H_2SO_4

FIGURE 2. AMMONIA MANIFOLD AA II

NITROGEN, AMMONIA

Method 350.2 (Colorimetric; Titrimetric; Potentiometric – Distillation Procedure)

STORET NO. Total 00610
Dissolved 00608

1. Scope and Application
   1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.
   1.2 The method covers the range from about 0.05 to 1.0 mg NH_3–N/1 for the colorimetric procedure, from 1.0 to 25 mg/1 for the titrimetric procedure, and from 0.05 to 1400 mg/1 for the electrode method.
   1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.
2. Summary of Method
   2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined colorimetrically by nesslerization, titrimetrically with standard sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.
3. Sample Handling and Preservation
   3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C.
4. Interferences
   4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.
   4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.
   4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

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5. Apparatus

5.1 An all-glass distilling apparatus with an 800–1000 ml flask.

5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.

5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm ±1.5 mm inside measurement from bottom.

5.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

NOTE 1: All solutions must be made with ammonia-free water.

6.2 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3–N. Dissolve 3.819 g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask.

6.3 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (6.2) to 1 liter in a volumetric flask.

6.4 Boric acid solution (20 g/1): Dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.

6.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethyl alcohol with 1 volume of 0.2% methylene blue in 95% ethyl alcohol. This solution should be prepared fresh every 30 days.

NOTE 2: Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95% ethanol.

6.6 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

NOTE 3: This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).

6.7 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7 \cdot 10H_2O$ per liter) and dilute to 1 liter.

6.8 Sulfuric acid, standard solution: (0.02 N, 1 ml = 0.28 mg NH_3–N). Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2-free distilled water.

NOTE 4: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can then be prepared.

6.8.1 Standardize the approximately 0.02 N acid against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1000 ml with CO_2-free distilled water.

6.9 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

6.10 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

a. Sodium thiosulfate (1/70 N): Dissolve 3.5 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter. One ml of this solution will remove 1 mg/1 of residual chlorine in 500 ml of sample.

b. Sodium arsenite (1/70 N): Dissolve 1.0 g $NaAsO_2$ in distilled water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7). Distill 300 ml at the rate of 6–10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

NOTE 5: The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution.

Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1 mg/1 the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically. The electrode method may also be used.

7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically or potentiometrically as described below.

7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

7.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3–N	mg NH_3–N/50.0 ml
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

Dilute each tube to 50 ml with distilled water, add 2.0 ml of Nessler reagent (6.6) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained plot absorbance vs. mg NH_3–N for the standard curve. Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the absorbance at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

7.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Selective Ion Electrode Method (Method 350.3) in this manual.

7.5 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

8. Calculations

8.1 Titrimetric

$$\text{mg/l } NH_3 - N = \frac{A \times 0.28 \times 1{,}000}{S}$$

where:

A = ml 0.02 N H_2SO_4 used.

S = ml sample.

8.2 Spectrophotometric

$$\text{mg/l } NH_3 - N = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where:

A = mg NH_3–N read from standard curve.

B = ml total distillate collected, including boric acid and dilution.

C = ml distillate taken for nesslerization.

D = ml of original sample taken.

8.3 Potentiometric

$$\text{mg/l NH}_3 - \text{N} = \frac{500}{D} \times A$$

where:

A = mg NH_3–N/1 from electrode method standard curve.

D = ml of original sample taken.

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

Increment as Nitrogen, Ammonia mg N/liter	Precision as Standard Deviation mgN/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.21	0.122	−5.54	−0.01
0.26	0.070	−18.12	−0.05
1.71	0.244	+0.46	+0.01
1.92	0.279	−2.01	−0.04

(FWPCA Method Study 2, Nutrient Analyses)

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NITROGEN, AMMONIA

Method 350.3 (Potentiometric, Ion Selective Electrode)

STORET NO. Total 00610
Dissolved 00608

1. Scope and Application
   - 1.1 This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 This method covers the range from 0.03 to 1400 mg NH_3–N/1. Color and turbidity have no effect on the measurements, thus, distillation may not be necessary.
2. Summary of Method
   - 2.1 The ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter.
   - 2.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.
3. Sample Handling and Preservation
   - 3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C.
4. Interferences
   - 4.1 Volatile amines act as a positive interference.
   - 4.2 Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.
5. Apparatus
   - 5.1 Electrometer (pH meter) with expanded mV scale or a specific ion meter.
   - 5.2 Ammonia selective electrode, such as Orion Model 95–10 or EIL Model 8002–2.
   - 5.3 Magnetic stirrer, thermally insulated, and Teflon-coated stirring bar.
6. Reagents
   - 6.1 Distilled water: Special precautions must be taken to insure that the distilled water is free of ammonia. This is accomplished by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.
   - 6.2 Sodium hydroxide, 10N: Dissolve 400 g of sodium hydroxide in 800 ml of distilled water. Cool and dilute to 1 liter with distilled water (6.1).
   - 6.3 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3–N. Dissolve 3.819 g NH_4Cl in water and bring to volume in a 1 liter volumetric flask using distilled water (6.1).

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6.4 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg NH_3–N. Dilute 10.0 ml of the stock solution (6.3) to 1 liter with distilled water (6.1) in a volumetric flask.

NOTE 1: When analyzing saline waters, standards must be made up in synthetic ocean water (SOW); found in Nitrogen, Ammonia: Colorimetric, Automated Phenate Method (350.1).

7. Procedure

7.1 Preparation of standards: Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium chloride.

7.2 Calibration of electrometer: Place 100 ml of each standard solution in clean 150 ml beakers. Immerse electrode into standard of lowest concentration and add 1 ml of 10N sodium hydroxide solution while mixing. Keep electrode in the solution until a stable reading is obtained.

NOTE 2: The pH of the solution after the addition of NaOH must be above 11.

Caution: Sodium hydroxide must not be added prior to electrode immersion, for ammonia may be lost from a basic solution.

7.3 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Using semilogarithmic graph paper, plot the concentration of ammonia in mg NH_3–N/1 on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

7.4 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

7.5 Sample measurement: Follow the procedure in (7.2) for 100 ml of sample in 150 ml beakers. Record the stabilized potential of each unknown sample and convert the potential reading to the ammonia concentration using the standard curve. If a specific ion meter is used, read the ammonia level directly in mg NH_3–N/1.

8. Precision and Accuracy

8.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg NH_3–N/1, standard deviations were ±0.038, ±0.017, ±0.007, and ±0.003, respectively.

8.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.19 and 0.13 mg NH_3–N/1, recoveries were 96% and 91%, respectively.

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NITROGEN, KJELDAHL, TOTAL

Method 351.1 (Colorimetric, Automated Phenate)

STORET NO. 00625

1. Scope and Application

   1.1 This automated method may be used to determine Kjeldahl nitrogen in surface and saline waters. The applicable range is 0.05 to 2.0 mg N/1. Approximately 20 samples per hour can be analyzed.

2. Summary of Method

   2.1 The sample is automatically digested with a sulfuric acid solution containing potassium sulfate and mercuric sulfate as a catalyst to convert organic nitrogen to ammonium sulfate. The solution is then automatically neutralized with sodium hydroxide solution and treated with alkaline phenol reagent and sodium hypochlorite reagent. This treatment forms a blue color designated as indophenol. Sodium nitroprusside, which increases the intensity of the color, is added to obtain necessary sensitivity for measurement of low level nitrogen.

3. Definitions

   3.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and of organic nitrogen compounds which are converted to $(NH_4)_2SO_4$ under the conditions of digestion which are specified below.

   3.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value from the total Kjeldahl nitrogen value. Also, organic Kjeldahl nitrogen may be determined directly by removal of ammonia before digestion.

4. Sample Handling and Preservation

   4.1 Samples may be preserved by addition of 2 ml of conc. H_2SO_4 per liter and refrigeration at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Therefore, samples should be analyzed as soon as possible.

5. Interferences

   5.1 Iron and chromium ions tend to catalyze while copper ions tend to inhibit the indophenol color reaction.

6. Apparatus

   6.1 Technicon AutoAnalyzer consisting of:

      6.1.1 Sampler II, equipped with continuous mixer.
      6.1.2 Two proportioning pumps.
      6.1.3 Manifold I.
      6.1.4 Manifold II.
      6.1.5 Continuous digester.
      6.1.6 Planetary pump.

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6.1.7 Five-gallon Carboy fume-trap.

6.1.8 80°C Heating bath.

6.1.9 Colorimeter equipped with 50 mm tubular flow cell and 630 nm filters.

6.1.10 Recorder equipped with range expander.

6.1.11 Vacuum pump.

7. Reagents

7.1 Distilled water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. Furthermore, since organic contamination may interfere with this analysis, use of the resin Dowex XE-75 or equivalent which also tends to remove organic impurities is advised. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer.

NOTE 1: All solutions must be made using ammonia-free water.

7.2 Sulfuric acid: As it readily absorbs ammonia, special precaution must also be taken with respect to its use. Do not store bottles reserved for this determination in areas of potential ammonia contamination.

7.3 EDTA (2% solution): Dissolve 20 g disodium ethylenediamine tetraacetate in 1 liter of distilled water. Adjust pH to 10.5–11 with NaOH (7.4).

7.4 Sodium hydroxide (30% solution): Dissolve 300 g NaOH in 1 liter of distilled water.

NOTE 2: The 30% sodium hydroxide should be sufficient to neutralize the digestate. In rare cases it may be necessary to increase the concentration of sodium hydroxide in this solution to insure neutralization of the digested sample in the manifold at the water jacketed mixing coil.

7.5 Sodium nitroprusside, (0.05% solution): Dissolve 0.5 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in 1 liter distilled water.

7.6 Alkaline phenol reagent: Pour 550 ml liquid phenol (88–90%) slowly with mixing into 1 liter of 40% (400 g per liter) NaOH. Cool and dilute to 2 liters with distilled water.

7.7 Sodium hypochlorite (1% solution): Dilute commercial "Clorox"–200 ml to 1 liter with distilled water. Available chlorine level should be approximately 1%. Due to the instability of this product, storage over an extended period should be avoided.

7.8 Digestant mixture: Place 2 g red HgO in a 2 liter container. Slowly add, with stirring, 300 ml of acid water (100 ml H_2SO_4 + 200 ml H_2O) and stir until cool. Add 100 ml 10% (10 g per 100 ml) K_2SO_4. Dilute to 2 liters with conc. sulfuric acid (approximately 500 ml at a time, allowing time for cooling). Allow 4 hours for the precipitate to settle or filter through glass fiber filter.

7.9 Stock solution: Dissolve 4.7193 g of pre-dried (1 hour at 105°C) ammonium sulfate in distilled water and dilute to 1.0 liter in a volumetric flask. 1.0 ml = 1.0 mg N.

7.10 Standard solution: Dilute 10.0 ml of stock solution (7.9) to 1000 ml. 1.0 ml = 0.01 mg N.

7.11 Using the standard solution (7.10), prepare the following standards in 100 ml volumetric flasks:

Conc., mg N/l	ml Standard Solution/100 ml
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.40	4.0
0.60	6.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

8. Procedure

8.1 Set up manifolds as shown in Figures 1, 2, and 3.

8.1.1 In the operation of manifold No. 1, the control of four key factors is required to enable manifold No. 2 to receive the mandatory representative feed. First, the digestant flowing into the pulse chamber (PC-1) must be bubble free; otherwise, air will accumulate in A-7, thus altering the ratio of sample to digestant in digestor. Second, in maintaining even flow from the digestor helix, the peristaltic pump must be adjusted to cope with differences in density of the digestate and the wash water. Third, the sample pick-up rate from the helix must be precisely adjusted to insure that the entire sample is aspirated into the mixing chamber. And finally, the contents of the "Mixing Chamber" must be kept homogeneous by the proper adjustment of the air bubbling rate.

8.1.2 In the operation of manifold No. 2, it is important in the neutralization of the digested sample to adjust the concentration of the NaOH so that the waste from the C-3 debubbler is slightly acid to Hydrion B paper.

8.1.3 The digestor temperature is 390°C for the first stage and 360°C for the second and third stages.

8.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

8.3 Set sampling rate of Sampler II at 20 samples per hour, using a sample to wash ratio of 1 to 2 (1 minute sample, 2 minute wash).

8.4 Arrange various standards in sampler cups in order of increasing concentration. Complete loading of sampler tray with unknown samples.

8.5 Switch sample line from distilled water to sampler and begin analysis.

9. Calculation

9.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

9.2 Any sample that has a computed concentration that is less than 10% of the sample run immediately prior to it must be rerun.

10. Precision and Accuracy

10.1 Six laboratories analyzed four natural water samples containing exact increments of organic nitrogen compounds, with the following results:

Increment as Kjeldahl-Nitrogen mg N/liter	Precision as Standard Deviation Kjeldahl-N mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
1.89	0.54	-24.6	-0.46
2.18	0.61	-28.3	-0.62
5.09	1.25	-23.8	-1.21
5.81	1.85	-21.9	-1.27

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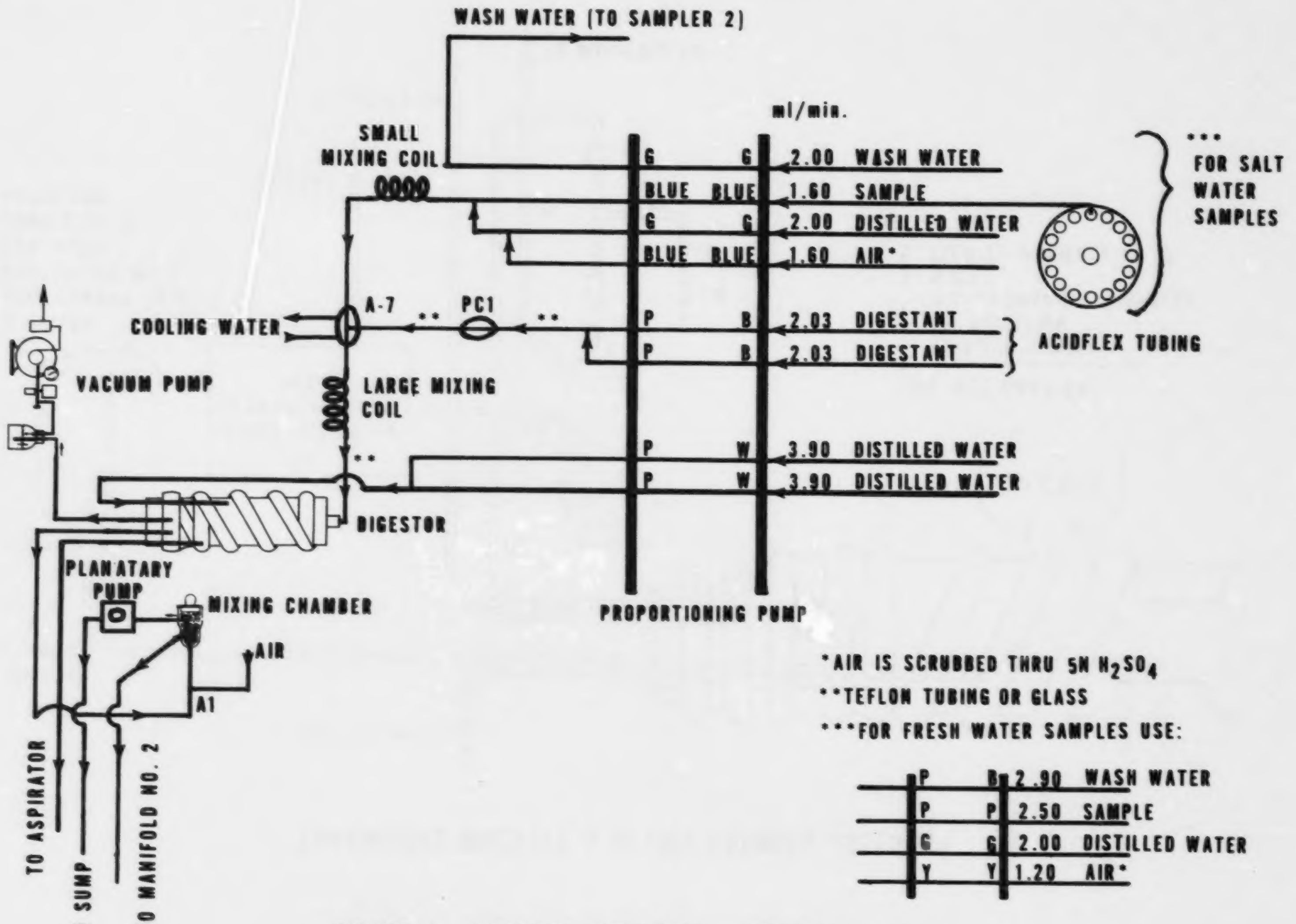
WASH WATER (TO SAMPLER 2)
ml/min.
SMALL MIXING COIL
G G 2.00 WASH WATER
BLUE BLUE 1.60 SAMPLE
G G 2.00 DISTILLED WATER
BLUE BLUE 1.60 AIR*
P B 2.03 DIGESTANT
P B 2.03 DIGESTANT
P W 3.90 DISTILLED WATER
P W 3.90 DISTILLED WATER
*** FOR SALT WATER SAMPLES
ACIDFLEX TUBING
A-7
PC1
**
COOLING WATER
VACUUM PUMP
LARGE MIXING COIL
DIGESTOR
PLANATARY PUMP
MIXING CHAMBER
AIR
A1
TO ASPIRATOR
TO SUMP
TO MANIFOLD NO. 2
PROPORTIONING PUMP
*AIR IS SCRUBBED THRU 5N H_2SO_4
**TEFLON TUBING OR GLASS
***FOR FRESH WATER SAMPLES USE:
P B 2.90 WASH WATER
P P 2.50 SAMPLE
G G 2.00 DISTILLED WATER
Y Y 1.20 AIR*

FIGURE 1. KJELDAHL NITROGEN – MANIFOLD 1 AA-I

CONTINUOUS DIGESTER & MIXING CHAMBER ASSEMBLY

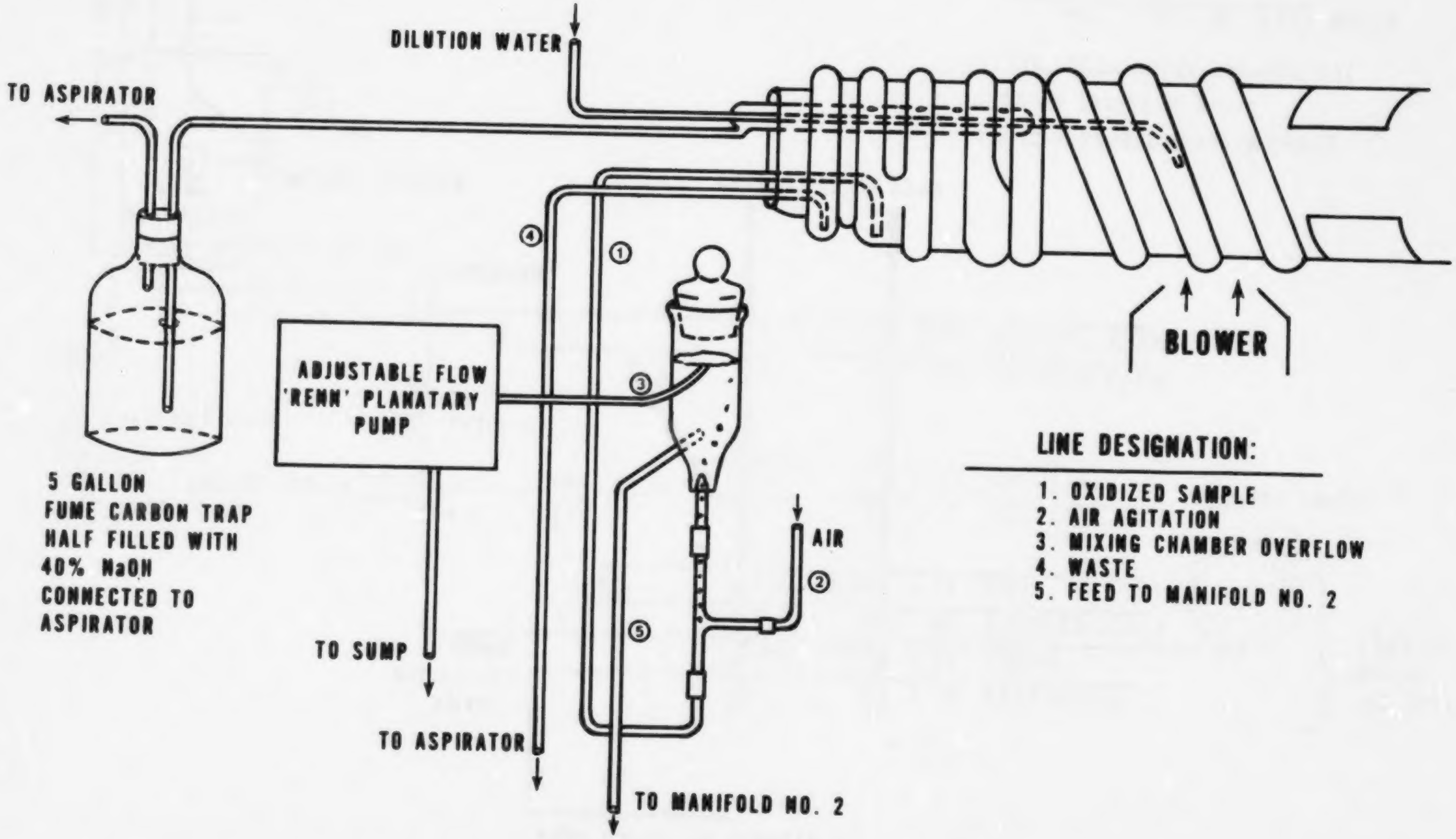
DILUTION WATER
TO ASPIRATOR
5 GALLON
FUME CARBON TRAP
HALF FILLED WITH
40% NaOH
CONNECTED TO
ASPIRATOR
ADJUSTABLE FLOW
'RENN' PLANATARY
PUMP
TO SUMP
TO ASPIRATOR
TO MANIFOLD NO. 2
AIR
①
②
③
④
⑤
BLOWER
LINE DESIGNATION:
1. OXIDIZED SAMPLE
2. AIR AGITATION
3. MIXING CHAMBER OVERFLOW
4. WASTE
5. FEED TO MANIFOLD NO. 2

FIGURE 2. KJELDAHL NITROGEN AA-I

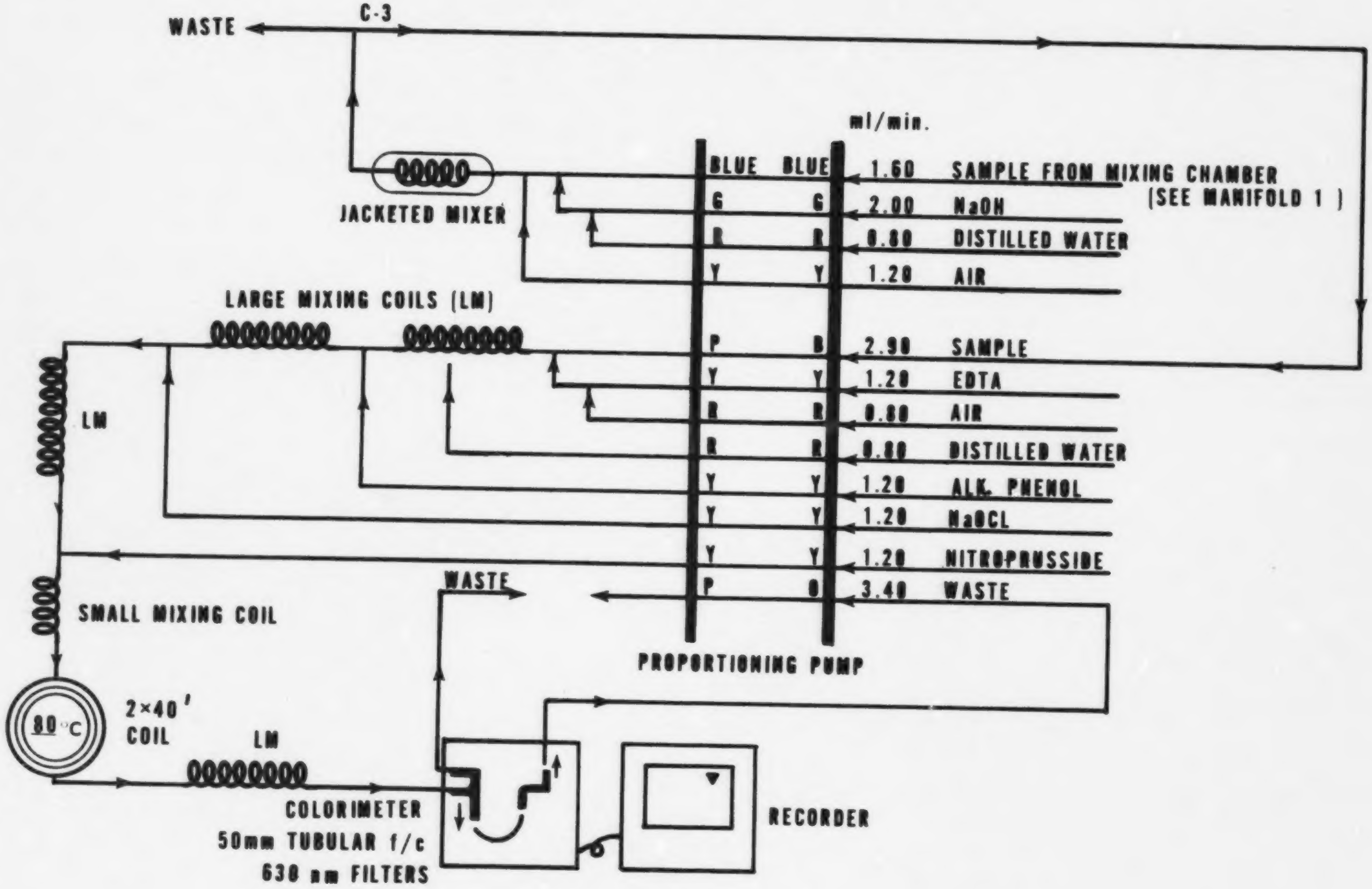
WASTE
C-3
ml/min.
JACKETED MIXER
BLUE BLUE 1.60 SAMPLE FROM MIXING CHAMBER (SEE MANIFOLD 1)
G G 2.00 NaOH
R R 0.80 DISTILLED WATER
Y Y 1.20 AIR
P B 2.90 SAMPLE
Y Y 1.20 EDTA
R R 0.80 AIR
R R 0.80 DISTILLED WATER
Y Y 1.20 ALK. PHENOL
Y Y 1.20 NaOCL
Y Y 1.20 NITROPRUSSIDE
P O 3.40 WASTE
LARGE MIXING COILS (LM)
LM
SMALL MIXING COIL
WASTE
PROPORTIONING PUMP
80 °C
2×40' COIL
LM
COLORIMETER
50mm TUBULAR f/c
630 nm FILTERS
RECORDER

FIGURE 3. KJELDAHL NITROGEN MANIFOLD 2. AA-I

NITROGEN, KJELDAHL, TOTAL

Method 351.2 (Colorimetric, Semi-Automated Block Digester, AAII)

STORET NO. 00625

1. Scope and Application

1.1 This method covers the determination of total Kjeldahl nitrogen in drinking and surface waters, domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogeneous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines. The applicable range of this method is 0.1 to 20 mg/1 TKN. The range may be extended with sample dilution.

2. Summary of Method

2.1 The sample is heated in the presence of sulfuric acid, K_2SO_4 and $HgSO_4$ for two and one half hours. The residue is cooled, diluted to 25 ml and placed on the AutoAnalyzer for ammonia determination. This digested sample may also be used for phosphorus determination.

3. Definitions

3.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.

3.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value (Method 350.2, Nitrogen, Ammonia, this manual) from the total Kjeldahl nitrogen value.

4. Sample Handling and Preservation

4.1 Samples may be preserved by addition of 2 ml of conc H_2SO_4 per liter and stored at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Therefore, samples should be analyzed as soon as possible.

5. Apparatus

5.1 Block Digestor–40

5.2 Technicon Manifold for Ammonia (Figure 1)

5.3 Chemware TFE (Teflon boiling stones), Markson Science, Inc., Box 767, Delmar, CA 92014)

6. Reagents

6.1 Mercuric Sulfate: Dissolve 8 g red mercuric oxide (HgO) in 50 ml of 1:4 sulfuric acid (10 ml conc H_2SO_4: 40 ml distilled water) and dilute to 100 ml with distilled water.

6.2 Digestion Solution: (Sulfuric acid-mercuric sulfate-potassium sulfate solution): Dissolve 133 g of K_2SO_4 in 700 ml of distilled water and 200 ml of conc H_2SO_4. Add 25 ml of mercuric sulfate solution and dilute to 1 liter.

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6.3 Sulfuric Acid Solution (4%): Add 40 ml of conc. sulfuric acid to 800 ml of ammonia free distilled water, cool and dilute to 1 liter.

6.4 Stock Sodium Hydroxide (20%): Dissolve 200 g of sodium hydroxide in 900 ml of ammonia-free distilled water and dilute to 1 liter.

6.5 Stock Sodium Potassium Tartrate Solution (20%): Dissolve 200 g sodium potassium tartrate in about 800 ml of ammonia-free distilled water and dilute to 1 liter.

6.6 Stock Buffer Solution: Dissolve 134.0 g of sodium phosphate, dibasic (Na_2HPO_4) in about 800 ml of ammonia free water. Add 20 g of sodium hydroxide and dilute to 1 liter.

6.7 Working Buffer Solution: Combine the reagents in the stated order; add 250 ml of stock sodium potassium tartrate solution (6.5) to 200 ml of stock buffer solution (6.6) and mix. Add xx ml sodium hydroxide solution (6.4) and dilute to 1 liter. See concentration ranges, Table I, for composition of working buffer.

6.8 Sodium Salicylate/Sodium Nitroprusside Solution: Dissolve 150 g of sodium salicylate and 0.3 g of sodium nitroprusside in about 600 ml of ammonia free water and dilute to 1 liter.

6.9 Sodium Hypochlorite Solution: Dilute 6.0 ml sodium hypochlorite solution (clorox) to 100 ml with ammonia free distilled water.

6.10 Ammonium chloride, stock solution: Dissolve 3.819 g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask. 1 ml = 1.0 mg NH_3-N.

7. Procedure

Digestion

7.1 To 20 or 25 ml of sample, add 5 ml of digestion solution (6.2) and mix (use a vortex mixer).

7.2 Add (4–8) Teflon boiling stones (5.3). Too many boiling chips will cause the sample to boil over.

7.3 With Block Digestor in manual mode set low and high temperature at 160°C and preheat unit to 160°C. Place tubes in digestor and switch to automatic mode. Set low temperature timer for 1 hour. Reset high temperature to 380°C and set timer for 2 1/2 hours.

7.4 Cool sample and dilute to 25 ml with ammonia free water.

Colorimetric Analysis

7.5 Check the level of all reagent containers to ensure an adequate supply.

7.6 Excluding the salicylate line, place all reagent lines in their respective containers, connect the sample probe to the Sampler IV and start the proportioning pump.

7.7 Flush the Sampler IV wash receptacle with about 25 ml of 4.0% sulfuric acid (6.3).

7.8 When reagents have been pumping for at least five minutes, place the salicylate line in its respective container and allow the system to equilibrate. If a precipitate forms after the addition of salicylate, the pH is too low. Immediately stop the proportioning pump and flush the coils with water using a syringe. Before restarting the system, check the concentration of the sulfuric acid solutions and/or the working buffer solution.

TABLE 1

CONCENTRATION RANGES
(NITROGEN)

	Dilution loops						
	Initial sample		Resample				
No.	Sample line	Diluent line	Resample line	Diluent line	Approx. std. cal. setting	Range PPM N (±10%)	ml stock NaOH per liter working buffer solution
1	.80 (RED/RED)	.80 (RED/RED)	.32 (BLK/BLK)	.80 (RED/RED)	700	0–0.5	250
2	.80 (RED/RED)	.80 (RED/RED)	.32 (BLK/BLK)	.80 (RED/RED)	100	0–1.5	250
3	.16 (ORN/YEL)	.80 (RED/RED)	.32 (BLK/BLK)	.80 (RED/RED)	700	0–1	120
4	.16 (ORN/YEL)	.80 (RED/RED)	.32 (BLK/BLK)	.80 (RED/RED)	100	0–5	120
5	.16 (ORN/YEL)	.80 (RED/RED)	.16 (ORN/YEL)	.80 (RED/RED)	700	0–2	80
6	.16 (ORN/YEL)	.80 (RED/RED)	.16 (ORN/YEL)	.80 (RED/RED)	100	0–10	80

7.9 To prevent precipitation of sodium salicylate in the waste tray, which can clog the tray outlet, keep the nitrogen flowcell pump tube and the nitrogen Colorimeter "To Waste" tube separate from all other lines or keep tap water flowing in the waste tray.

7.10 After a stable baseline has been obtained start the Sampler.

8. Calculations

8.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentrations by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using sewage samples of concentrations of 1.2, 2.6, and 1.7 mg N/1, the precision was ±0.07, ±0.03 and ±0.15, respectively.

9.2 In a single laboratory (EMSL), using sewage samples of concentrations of 4.7 and 8.74 mg N/1, the recoveries were 99 and 99%, respectively.

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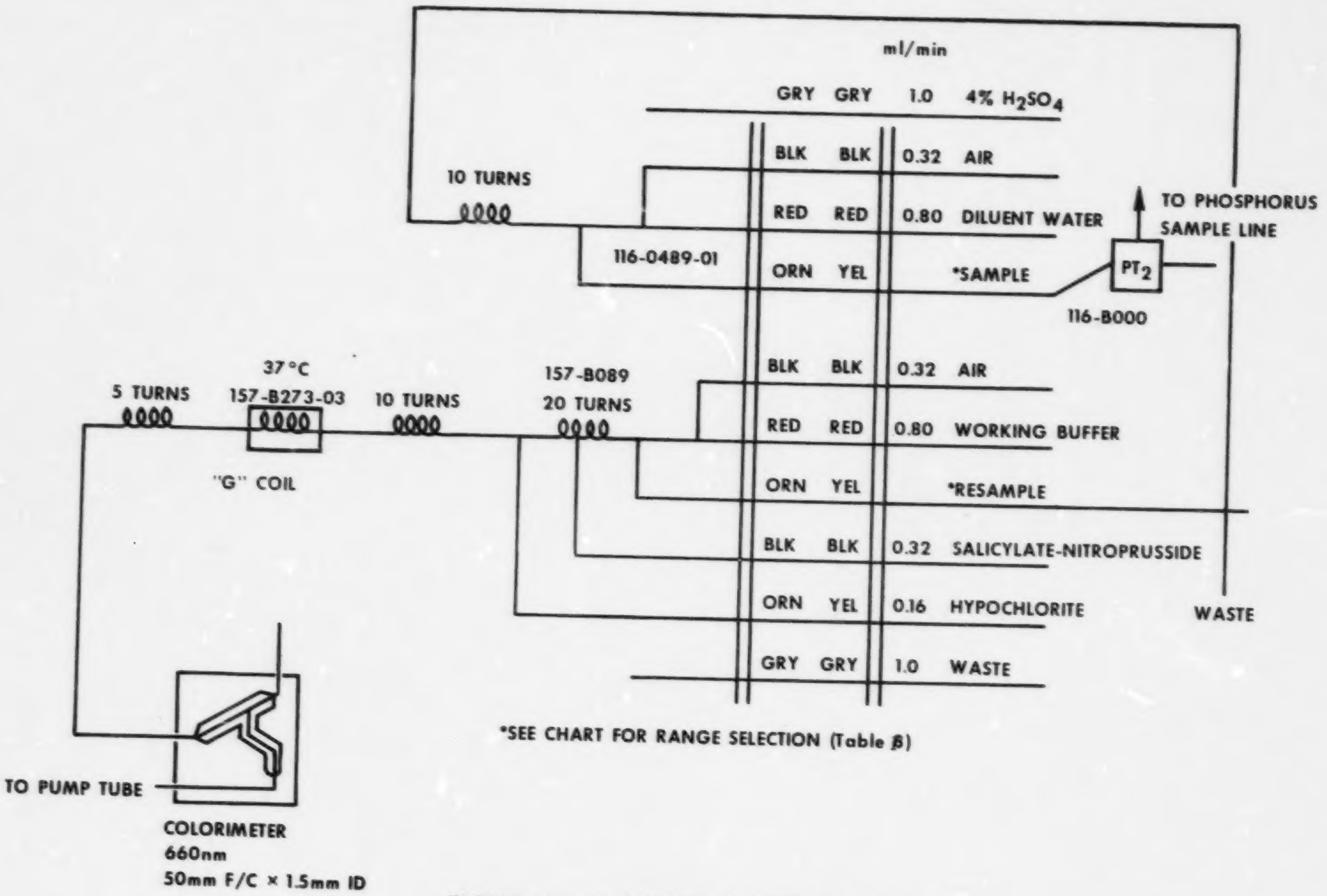

ml/min
GRY GRY 1.0 4% H_2SO_4
BLK BLK 0.32 AIR
RED RED 0.80 DILUENT WATER
ORN YEL *SAMPLE
BLK BLK 0.32 AIR
RED RED 0.80 WORKING BUFFER
ORN YEL *RESAMPLE
BLK BLK 0.32 SALICYLATE-NITROPRUSSIDE
ORN YEL 0.16 HYPOCHLORITE
GRY GRY 1.0 WASTE
10 TURNS
116-0489-01
TO PHOSPHORUS
SAMPLE LINE
PT_2
116-B000
WASTE
5 TURNS
37 °C
157-B273-03
10 TURNS
157-B089
20 TURNS
"G" COIL
TO PUMP TUBE
COLORIMETER
660nm
50mm F/C × 1.5mm ID

*SEE CHART FOR RANGE SELECTION (Table β)

FIGURE 1. AMMONIA MANIFOLD AAII

NITROGEN, KJELDAHL, TOTAL

Method 351.3 (Colorimetric; Titrimetric; Potentiometric)

STORET NO. 00625

1. Scope and Application
   - 1.1 This method covers the determination of total Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.
   - 1.2 Three alternatives are listed for the determination of ammonia after distillation: the titrimetric method which is applicable to concentrations above 1 mg N/liter; the Nesslerization method which is applicable to concentrations below 1 mg N/liter; and the potentiometric method applicable to the range 0.05 to 1400 mg/1.
   - 1.3 This method is described for macro and micro glassware systems.
2. Definitions
   - 2.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.
   - 2.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value (Method 350.2, Nitrogen, Ammonia, this manual) from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion.
3. Summary of Method
   - 3.1 The sample is heated in the presence of conc. sulfuric acid, K_2SO_4 and $HgSO_4$ and evaporated until SO_3 fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation by Nesslerization, titration or potentiometry.
4. Sample Handling and Preservation
   - 4.1 Samples may be preserved by addition of 2 ml of conc. H_2SO_4 per liter and stored at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.
5. Interference
   - 5.1 High nitrate concentrations (10X or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

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6. **Apparatus**

6.1 Digestion apparatus: A Kjeldahl digestion apparatus with 800 or 100 ml flasks and suction takeoff to remove SO_3 fumes and water.

6.2 Distillation apparatus: The macro Kjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected. Micro Kjeldahl steam distillation apparatus is commercially available.

6.3 Spectrophotometer for use at 400 to 425 nm with a light path of 1 cm or longer.

7. **Reagents**

7.1 Distilled water should be free of ammonia. Such water is best prepared by the passage of distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

NOTE 1: All solutions must be made with ammonia-free water.

7.2 Mercuric sulfate solution: Dissolve 8 g red mercuric oxide (HgO) in 50 ml of 1:4 sulfuric acid (10.0 ml conc. H_2SO_4 : 40 ml distilled water) and dilute to 100 ml with distilled water.

7.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution: Dissolve 267 g K_2SO_4 in 1300 ml distilled water and 400 ml conc. H_2SO_4. Add 50 ml mercuric sulfate solution (7.2) and dilute to 2 liters with distilled water.

7.4 Sodium hydroxide-sodium thiosulfate solution: Dissolve 500 g NaOH and 25 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter.

7.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethanol with 1 volume of 0.2% methylene blue in ethanol. Prepare fresh every 30 days.

7.6 Boric acid solution: Dissolve 20 g boric acid, H_3BO_3, in water and dilute to 1 liter with distilled water.

7.7 Sulfuric acid, standard solution: (0.02 N) 1 ml = 0.28 mg NH_3–N. Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2-free distilled water. Standardize the approximately 0.02 N acid so prepared against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1 liter with CO_2-free distilled water.

NOTE 2: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can the be prepared.

7.8 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3–N. Dissolve 3.819 g NH_4Cl in water and make up to 1 liter in a volumetric flask with distilled water.

7.9 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg NH_3–N. Dilute 10.0 ml of the stock solution (7.8) with distilled water to 1 liter in a volumetric flask.

7.10 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g potassium iodide in a small volume of distilled water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of distilled water. Dilute the mixture to 1 liter. The solution is stable for at least one year if stored in a pyrex bottle out of direct sunlight.

NOTE 3: Reagents 7.7, 7.8, 7.9, and 7.10 are identical to reagents 6.8, 6.2, 6.3, and 6.6 described under Nitrogen, Ammonia (Colorimetric; Titrimetric; Potentiometric-Distillation Procedure, Method 350.2).

8. Procedure

8.1 The distillation apparatus should be pre-steamed before use by distilling a 1:1 mixture of distilled water and sodium hydroxide-sodium thiosulfate solution (7.4) until the distillate is ammonia-free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).

8.2 Macro Kjeldahl system

8.2.1 Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800 ml Kjeldahl flask. The sample size can be determined from the following table:

Kjeldahl Nitrogen in Sample, mg/l	Sample Size ml
0–5	500
5–10	250
10–20	100
20–50	50.0
50–500	25.0

Dilute the sample, if required, to 500 ml with distilled water, and add 100 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Continue heating for 30 additional minutes. Cool the residue and add 300 ml distilled water.

8.2.2 Make the digestate alkaline by careful addition of 100 ml of sodium hydroxide – thiosulfate solution (7.4) without mixing.

NOTE 5: Slow addition of the heavy caustic solution down the tilted neck of the digestion flask will cause heavier solution to underlay the aqueous sulfuric acid solution without loss of free-ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.2.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask.

8.2.4 Distill 300 ml at the rate of 6–10 ml/min., into 50 ml of 2% boric acid (7.6) contained in a 500 ml Erlenmeyer flask.

8.2.5 Dilute the distillate to 500 ml in the flask. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks. For concentrations above 1 mg/1, the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/1.

8.3 Micro Kjeldahl system

8.3.1 Place 50.0 ml of sample or an aliquot diluted to 50 ml in a 100 ml Kjeldahl flask and add 10 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Then digest for an additional 30 minutes. Cool the residue and add 30 ml distilled water.

8.3.2 Make the digestate alkaline by careful addition of 10 ml of sodium hydroxide-thiosulfate solution (7.4) without mixing. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.3.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask or 50 ml short-form Nessler tube.

8.3.4 Steam distill 30 ml at the rate of 6–10 ml/min., into 5 ml of 2% boric acid (7.6).

8.3.5 Dilute the distillate to 50 ml. For concentrations above 1 mg/1 the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/1.

8.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically, or potentiometrically, as described below.

8.4.1 Titrimetric determination: Add 3 drops of the mixed indicator (7.5) to the distillate and titrate the ammonia with the 0.02 N H_2SO_4 (7.7), matching the endpoint against a blank containing the same volume of distilled water and H_3BO_3 (7.6) solution.

8.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3–N	mg NH_3–N/50.0 ml
0.0	0.0
0.5	0.005
1.0	0.010
2.0	0.020
4.0	0.040
5.0	0.050
8.0	0.080
10.0	0.10

Dilute each tube to 50 ml with ammonia free water, add 1 ml of Nessler Reagent (7.10) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained for the standards plot absorbance vs. mg NH_3-N for the standard curve. Develop color in the 50 ml diluted distillate in exactly the same manner and read mg NH_3-N from the standard curve.

8.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Potentiometric, Ion Selective Electrode Method, (Method 350.3) in this manual.

8.4.4 It is not imperative that all standards be treated in the same manner as the samples. It is recommended that at least 2 standards (a high and low) be digested, distilled, and compared to similar values on the curve to insure that the digestion-distillation technique is reliable. If treated standards do not agree with untreated standards the operator should find the cause of the apparent error before proceeding.

9. Calculation

9.1 If the titrimetric procedure is used, calculate Total Kjeldahl Nitrogen, in mg/1, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{(A - B)N \times F \times 1{,}000}{S}$$

where:

A = milliliters of standard 0.020 N H_2SO_4 solution used in titrating sample.
B = milliliters of standard 0.020 N H_2SO_4 solution used in titrating blank.
N = normality of sulfuric acid solution.
F = milliequivalent weight of nitrogen (14 mg).
S = milliliters of sample digested.

If the sulfuric acid is exactly 0.02 N the formula is shortened to:

$$\text{TKN, mg/l} = \frac{(A - B) \times 280}{S}$$

9.2 If the Nessler procedure is used, calculate the Total Kjeldahl Nitrogen, in mg/1, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where:

A = mg NH_3–N read from curve.
B = ml total distillate collected including the H_3BO_3.
C = ml distillate taken for Nesslerization.
D = ml of original sample taken.

9.3 Calculate Organic Kjeldahl Nitrogen in mg/1, as follows:
Organic Kjeldahl Nitrogen = TKN –(NH_3–N.)

9.4 Potentiometric determination: Calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{B}{D} \times A$$

where:
A = mg NH_3–N/l from electrode method standard curve.
B = volume of diluted distillate in ml.
D = ml of original sample taken.

10. Precision

10.1 Thirty-one analysts in twenty laboratories analyzed natural water samples containing exact increments of organic nitrogen, with the following results:

Increment as Nitrogen, Kjeldahl mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.20	0.197	+15.54	+0.03
0.31	0.247	+ 5.45	+0.02
4.10	1.056	+ 1.03	+0.04
4.61	1.191	− 1.67	−0.08

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 437, Method 421 (1975).
2. Schlueter, Albert, "Nitrate Interference In Total Kjeldahl Nitrogen Determinations and Its Removal by Anion Exchange Resins", EPA Report 600/7–77–017.

NITROGEN, KJELDAHL, TOTAL

Method 351.4 (Potentiometric, Ion Selective Electrode)

STORET NO. 00625

1. Scope and Application
   - 1.1 This method is applicable to the measurement of TKN in drinking and surface water, domestic and industrial wastes.
   - 1.2 This method covers the range from 0.03 to 25 mg TKN/1.
2. Summary of Method
   - 2.1 Following digestion and cooling, distilled water is added to the digestion flask and the pH adjusted to between 3 and 4.5 by the addition of 10 N NaOH. The sample is cooled and transferred to a 100 ml beaker. After inserting the electrode into the sample, NaOH-NaI-EDTA is added and the ammonia measured. (Ethylene diamine tetraacetic acid (EDTA) is added to the alkaline reagent (NaOH-NaI) to prevent precipitation of hydroxides, thereby avoiding deposition on the electrode membrane).
3. Sample Handling and Preservation
   - 3.1 Samples may be preserved by addition of 2 ml of conc. H_2SO_4 per liter and stored at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.
4. Interferences
   - 4.1 Interference from metals is eliminated with the addition of NaI.
   - 4.2 High nitrate concentrations (10X or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.
5. Apparatus
   - 5.1 Electrometer (pH meter) with expanded mV scale.
   - 5.2 Ammonia selective electrode, such as Orion Model 95–10.
   - 5.3 Magnetic stirrer, thermally insulated and Teflon-coated stirring bar.
   - 5.4 Digestion apparatus: A Kjeldahl digestion apparatus with 800 or 100 ml flasks and suction take off to remove SO_3 fumes and water.
   - 5.5 Technicon Block Digestor BD-40.
6. Reagents
   - 6.1 Distilled water should be free of ammonia. Such water is best prepared by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

     NOTE 1: All solutions must be made with ammonia-free water.
   - 6.2 Mercuric sulfate solution: Dissolve 8 g red mercuric oxide (HgO) in 50 ml of 1:4 sulfuric acid (10.0 ml conc H_2SO_4: 40 ml distilled water) and dilute to 100 ml with distilled water.

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6.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution: Dissolve 267 g K_2SO_4 in 1300 ml distilled water and 400 ml conc H_2SO_4. Add 50 ml mercuric sulfate solution (6.2) and dilute to 2 liters with distilled water.

6.4 Sodium hydroxide 10N: Dissolve 400 g NaOH in 600 ml of ammonia-free water, cool and dilute to 1 liter.

6.5 Sodium Hydroxide, Sodium Iodide and EDTA Solution: Dissolve 400 g of NaOH, 300 g NaI and 2 g of EDTA in 700 ml of ammonia-free water, cool and dilute to 1 liter.

6.6 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3-N. Dissolve 3.819 g NH_4Cl in water and make up to 1 liter in a volumetric flask with distilled water.

6.7 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg NH_3-N. Dilute 10.0 ml of the stock solution (6.6) to 1 liter with distilled water in a volumetric flask.

7. Procedure

7.1 Macro Kjeldahl system

7.7.1 Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800 ml Kjeldahl flask. The sample size can be determined from the following table:

Kjedahl Nitrogen in Sample, mg/l	Sample Size ml
0–5	500
5–10	250
10–20	100
20–50	50.0
50–500	25.0

Dilute the sample, if required, to 500 ml with distilled water, and add 100 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (6.3) and evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Continue heating for 30 additional minutes. Cool the residue and add 500 ml distilled water and mix.

7.2 Micro Kjeldahl system

7.2.1 Place 50.0 ml of sample, or an aliquot diluted to 50 ml, in a 100 ml Kjeldahl flask and add 10 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (6.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Then digest for an additional 30 minutes. Cool the residue, add 44 ml distilled water and mix.

7.3 Block Digestor

7.3.1 Place 20 ml of sample, or an aliquot diluted to 20 ml, in the digestion tube. Add 5 ml of sulfuric acid-mercuric sulfate-potassium sulfate solution (6.3) and mix. Add 4–8 Teflon boiling stones.

7.3.2 Place tubes in digestor that has been preheated to 200°C.

7.3.3 Set low temperature at 200°C for 1 hour, the high temperature at 380°C and total time for two and one half hours.

7.3.4 After the temperature of the block has reached 380°C, the time should be set for 30 minutes. Longer time and higher temperature may result in complete loss of the acid.

7.3.5 Cool, add 25 ml of ammonia-free water and mix.

7.4 Electrode analysis

7.4.1 All standards should be treated as the samples and should contain the same concentration of sulfuric acid-mercuric sulfate-potassium sulfate solution (6.3).

7.4.2 Macro Kjeldahl system

To a 100 ml aliquot, add 15 ml of 10 N NaOH (6.4), mix and cool to room temperature. Immerse the electrode in the sample solution and add 4 ml of NaOH-NaI-EDTA reagent (6.5) while mixing. Allow the electrode to remain immersed in the solution until a stable reading is obtained.

7.4.3 Micro Kjeldahl system

Add 6 ml of 10 N NaOH solution (6.4), cool to room temperature and transfer the sample to a 100 ml beaker. Immerse the electrode in the sample solution and add 4 ml of NaOH-NaI-EDTA reagent (6.5) while mixing. Allow the electrode to remain immersed in the solution until a stable reading is obtained.

7.4.4 Block Digestor

Add 3 ml of 10 N NaOH (6.4), cool to room temperature, dilute to 50 ml and transfer to a 100 ml beaker. Immerse the electrode in the sample and add 2 ml of NaOH-NaI-EDTA reagent (6.5) while mixing. Allow the electrode to remain immersed in the solution until a stable reading is obtained.

8. Calculation

Using semilogarithmic graph paper, plot the concentration of ammonia in mg NH_3-N on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

$$\text{mg TKN/l} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = mg NH_3-N read from standard curve

B = mg NH_3-N in blank

C = ml of original sample taken

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

Bibliography

1. Schlueter, A., "Nitrate Interference in Total Kjeldahl Nitrogen Determinations and its Removal by Anion Exchange Resin", EPA-600/7–77–017.

NITROGEN, NITRATE

Method 352.1 (Colorimetric, Brucine)

STORET NO. Total 00620

1. Scope and Application
   1.1 This method is applicable to the analysis of drinking, surface and saline waters, domestic and industrial wastes. Modification can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample.
   1.2 The applicable range of concentrations is 0.1 to 2 mg NO_3–N/liter.
2. Summary of Method
   2.1 This method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N H_2SO_4 solution at a temperature of 100°C. The color of the resulting complex is measured at 410 nm. Temperature control of the color reaction is extremely critical.
3. Sample Handling and Preservation
   3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml conc. H_2SO_4 per liter) and refrigeration.
4. Interferences
   4.1 Dissolved organic matter will cause an off color in 13 N H_2SO_4 and must be compensated for by additions of all reagents except the brucine-sulfanilic acid reagent. This also applies to natural color present not due to dissolved organics.
   4.2 The effect of salinity is eliminated by addition of sodium chloride to the blanks, standards and samples.
   4.3 All strong oxidizing or reducing agents interfere. The presence of oxidizing agents may be determined with a total residual chlorine test kit.
   4.4 Residual chlorine interference is eliminated by the addition of sodium arsenite.
   4.5 Ferrous and ferric iron and quadrivalent manganese give slight positive interferences, but in concentrations less than 1 mg/1 these are negligible.
   4.6 Uneven heating of the samples and standards during the reaction time will result in erratic values. The necessity for absolute control of temperature during the critical color development period cannot be too strongly emphasized.
5. Apparatus
   5.1 Spectrophotometer or filter photometer suitable for measuring absorbance at 410 nm.
   5.2 Sufficient number of 40–50 ml glass sample tubes for reagent blanks, standards and samples.
   5.3 Neoprene coated wire racks to hold sample tubes.
   5.4 Water bath suitable for use at 100°C. This bath should contain a stirring mechanism so that all tubes are at the same temperature and should be of sufficient capacity to accept

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the required number of tubes without significant drop in temperature when the tubes are immersed.

5.5 Water bath suitable for use at 10–15°C.

6. Reagents

6.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.

6.2 Sodium chloride solution (30%): Dissolve 300 g NaCl in distilled water and dilute to 1 liter.

6.3 Sulfuric acid solution: Carefully add 500 ml conc. H_2SO_4 to 125 ml distilled water. Cool and keep tightly stoppered to prevent absorption of atmospheric moisture.

6.4 Brucine-sulfanilic acid reagent: Dissolve 1 g brucine sulfate $[(C_{23}H_{26}N_2O_4)_2 \cdot H_2SO_4 \cdot 7H_2O]$ and 0.1 g sulfanilic acid $(NH_2C_6H_4SO_3H \cdot H_2O)$ in 70 ml hot distilled water. Add 3 ml conc. HCl, cool, mix and dilute to 100 ml with distilled water. Store in a dark bottle at 5°C. This solution is stable for several months; the pink color that develops slowly does not effect its usefulness. Mark bottle with warning CAUTION: Brucine Sulfate is toxic; take care to avoid ingestion.

6.5 Potassium nitrate stock solution: 1.0 ml = 0.1 mg NO_3–N. Dissolve 0.7218 g anhydrous potassium nitrate (KNO_3) in distilled water and dilute to 1 liter in a volumetric flask. Preserve with 2 ml chloroform per liter. This solution is stable for at least 6 months.

6.6 Potassium nitrate standard solution: 1.0 ml = 0.001 mg NO_3–N. Dilute 10.0 ml of the stock solution (6.5) to 1 liter in a volumetric flask. This standard solution should be prepared fresh weekly.

6.7 Acetic acid (1 + 3): Dilute 1 volume glacial acetic acid (CH_3COOH) with 3 volumes of distilled water.

6.8 Sodium hydroxide (1N): Dissolve 40 g of NaOH in distilled water. Cool and dilute to 1 liter.

7. Procedure

7.1 Adjust the pH of the samples to approximately 7 with acetic acid (6.7) or sodium hydroxide (6.8). If necessary, filter to remove turbidity.

7.2 Set up the required number of sample tubes in the rack to handle reagent blank, standards and samples. Space tubes evenly throughout the rack to allow for even flow of bath water between the tubes. This should assist in achieving uniform heating of all tubes.

7.3 If it is necessary to correct for color or dissolved organic matter which will cause color on heating, a set of duplicate samples must be run to which all reagents except the brucine-sulfanilic acid have been added.

7.4 Pipette 10.0 ml of standards and samples or an aliquot of the samples diluted to 10.0 ml into the sample tubes.

7.5 If the samples are saline, add 2 ml of the 30% sodium chloride solution (6.2) to the reagent blank, standards and samples. For fresh water samples, sodium chloride solution may be omitted. Mix contents of tubes by swirling and place rack in cold water bath (0–10°C).

7.6 Pipette 10.0 ml of sulfuric acid solution (6.3) into each tube and mix by swirling. Allow tubes to come to thermal equilibrium in the cold bath. Be sure that temperatures have equilibrated in all tubes before continuing.

7.7 Add 0.5 ml brucine-sulfanilic acid reagent (6.4) to each tube (except the interference control tubes, 7.3) and carefully mix by swirling, then place the rack of tubes in the 100°C water bath for exactly 25 minutes.

Caution: Immersion of the tube rack into the bath should not decrease the temperature of the bath more than 1 to 2°C. In order to keep this temperature decrease to an absolute minimum, flow of bath water between the tubes should not be restricted by crowding too many tubes into the rack. If color development in the standards reveals discrepancies in the procedure, the operator should repeat the procedure after reviewing the temperature control steps.

7.8 Remove rack of tubes from the hot water bath and immerse in the cold water bath and allow to reach thermal equilibrium (20–25°C).

7.9 Read absorbance against the reagent blank at 410 nm using a 1 cm or longer cell.

8. Calculation

8.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against mg NO_3–N/1. (The color reaction does not always follow Beer's law).

8.2 Subtract the absorbance of the sample without the brucine-sulfanilic reagent from the absorbance of the sample containing brucine-sulfanilic acid and determine mg NO_3–N/1. Multiply by an appropriate dilution factor if less than 10 ml of sample is taken.

9. Precision and Accuracy

9.1 Twenty-seven analysts in fifteen laboratories analyzed natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrogen, Nitrate mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.16	0.092	–6.79	–0.01
0.19	0.083	+8.30	+0.02
1.08	0.245	+4.12	+0.04
1.24	0.214	+2.82	+0.04

(FWPCA Method Study 2, Nutrient Analyses).

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 427, Method 419D (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 992–71, p 363 (1976).
3. Jenkins, D., and Medsken, L., "A Brucine Method for the Determination of Nitrate in Ocean, Estuarine, and Fresh Waters", Anal Chem., 36, p 610, (1964).

NITROGEN, NITRATE–NITRITE

Method 353.1 (Colorimetric, Automated, Hydrazine Reduction)

STORET NO. Total 00630

1. Scope and Application
   1.1 This method is applicable to drinking and surface water, and domestic and industrial wastes. The applicable range of this method is 0.01–10 mg/1 nitrate-nitrite nitrogen. Approximately 20 samples per hour can be analyzed.
2. Summary of Method
   2.1 Nitrate is reduced to nitrite with hydrazine sulfate and the nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically.
3. Sample Handling and Preservation
   3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, samples should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with 2 ml of sulfuric acid (H_2SO_4) per liter and refrigerated.
4. Interferences
   4.1 Sample color that absorbs in the photometric range used for analysis will interfere.
   4.2 The apparent NO_3 and NO_2 concentrations varied ±10 percent with concentrations of sulfide ion up to 10 mg/1.
5. Apparatus
   5.1 Sampler
   5.2 Manifold AAI or AAII
   5.3 Proportioning Pump
   5.4 Heating bath 32°C AAI or 37°C AAII
   5.5 Continuous filter
   5.6 Colorimeter equipped with an 8 mm, 15 mm or 50 mm flow cell and 529 nm filters.
6. Reagents
   6.1 Color developing reagent: To approximately 500 ml of distilled water add 200 ml concentrated phosphoric acid (sp. gr. 1.834), 10 g sulfanilamide ($H_2NC_6H_4SO_2NH_2$) followed by 0.8 g N (1-Naphthyl) ethylenediamine dihydrochloride. Dilute the solution to 1 liter with distilled water and store in a dark bottle in the refrigerator. This solution is stable for approximately 1 month.
   6.2 Copper sulfate stock solution: Dissolve 2.5 g of copper sulfate ($CuSO_4 \cdot 5H_2O$) in distilled water and dilute to 1 liter.

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Reissued with revision 1978

6.3 Copper sulfate dilute solution: Dilute 20 ml of stock solution (6.2) to 2 liters with distilled water.

6.4 Sodium hydroxide stock solution, (10N): Dissolve 400 g NaOH in 750 ml distilled water, cool and dilute to 1 liter.

6.5 Sodium hydroxide (1.0N): Dilute 100 ml of stock NaOH solution (6.4) to 1 liter.

6.6 Hydrazine sulfate stock solution: Dissolve 27.5 g of hydrazine sulfate ($N_2H_4 \cdot H_2SO_4$) in 900 ml of distilled water and dilute to 1 liter. This solution is stable for approximately 6 months. CAUTION: Toxic if ingested. Mark container with appropriate warning.

6.7 Hydrazine sulfate dilute solution.

6.7.1 AAI: Dilute 55 ml of stock solution (6.6) to 1 liter.

6.7.2 AAII: Dilute 22 ml of stock solution (6.6) to 1 liter.

6.8 Stock nitrate solution (100 mg/1 NO_3-N): Dissolve 0.7218 g of KNO_3, oven dried at 100–105°C for 2 hours, in distilled water and dilute to 1 liter. Add 1 ml chloroform as a preservative. Stable for 6 months. 1 ml = 0.1 mg N.

6.9 Stock nitrite solution (100 mg/1 NO_2-N): Dissolve 0.6072 g KNO_2 in 500 ml of distilled water and dilute to 1 liter. Preserve with 2 ml of chloroform and keep under refrigeration. 1 ml = 0.1 mg N.

6.10 Standard nitrate solution: Dilute 100 ml of stock nitrate solution (6.8) to 1 liter. 1 ml = 0.01 mg N.

6.11 Using the stock nitrate solution (6.8), prepare the following standards in 100 ml volumetric flasks. At least one nitrite standard should be compared to a nitrate standard at the concentration to verify the efficiency of the reduction.

Conc., mg NO_3-N/l	ml of stock solution/100 ml
0.5	0.5
1.0	1.0
2.0	2.0
3.0	3.0
4.0	4.0
5.0	5.0
8.0	8.0
10.0	10.0

For standards in the range of 0.01 mg/1 use the standard nitrate solution.

7. Procedure

7.1 Set up the manifold as shown in Figure 1 (AAI) or Figure 2 (AAII). The continuous filter must be used to remove the precipitate.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line.

7.3 Run a 2.0 mg/1 NO_3-N and a 2.0 mg/1 NO_2-N standard through the system to check for 100% reduction of nitrate to nitrite. The two peaks should be of equal height. If they are not, the concentration of the hydrazine sulfate solution must be adjusted as follows. If the NO_3 peak is lower than that of the NO_2 peak the concentration of hydrazine sulfate should be increased until they are equal. If the NO_3 peak is higher than the nitrite, the concentration of the hydrazine sulfate should be reduced. When the correct concentration of hydrazine sulfate has been determined, no further adjustment should be necessary.

7.4 Place appropriate nitrate standards in the sampler in order of decreasing concentration of nitrogen. Complete loading tray with unknown samples.

7.5 For both the AAI and the AAII use a 2 minute sampling rate.

8. Calculation

8.1 Prepare a standard curve by plotting peak heights of processed standards against known concentrations. Compute concentrations of samples by comparing sample peak heights with the standard curve.

9. Precision and Accuracy

9.1 In a single laboratory using drinking water, surface water and industrial waste at concentrations of 0.39, 1.15, 1.76 and 4.75 *ug* NO_3-N/1, the standard deviations were ±0.02, ±0.01, ±0.02 and ±0.03, respectively. In a single laboratory using drinking water at concentrations of 0.75 and 2.97 the recoveries were 99% and 101%.

Bibliography

1. Kamphake, L., Hannah, S., and Cohen, J., "Automated Analysis For Nitrate by Hydrazine Reduction", Water Research 1, 205 (1967)

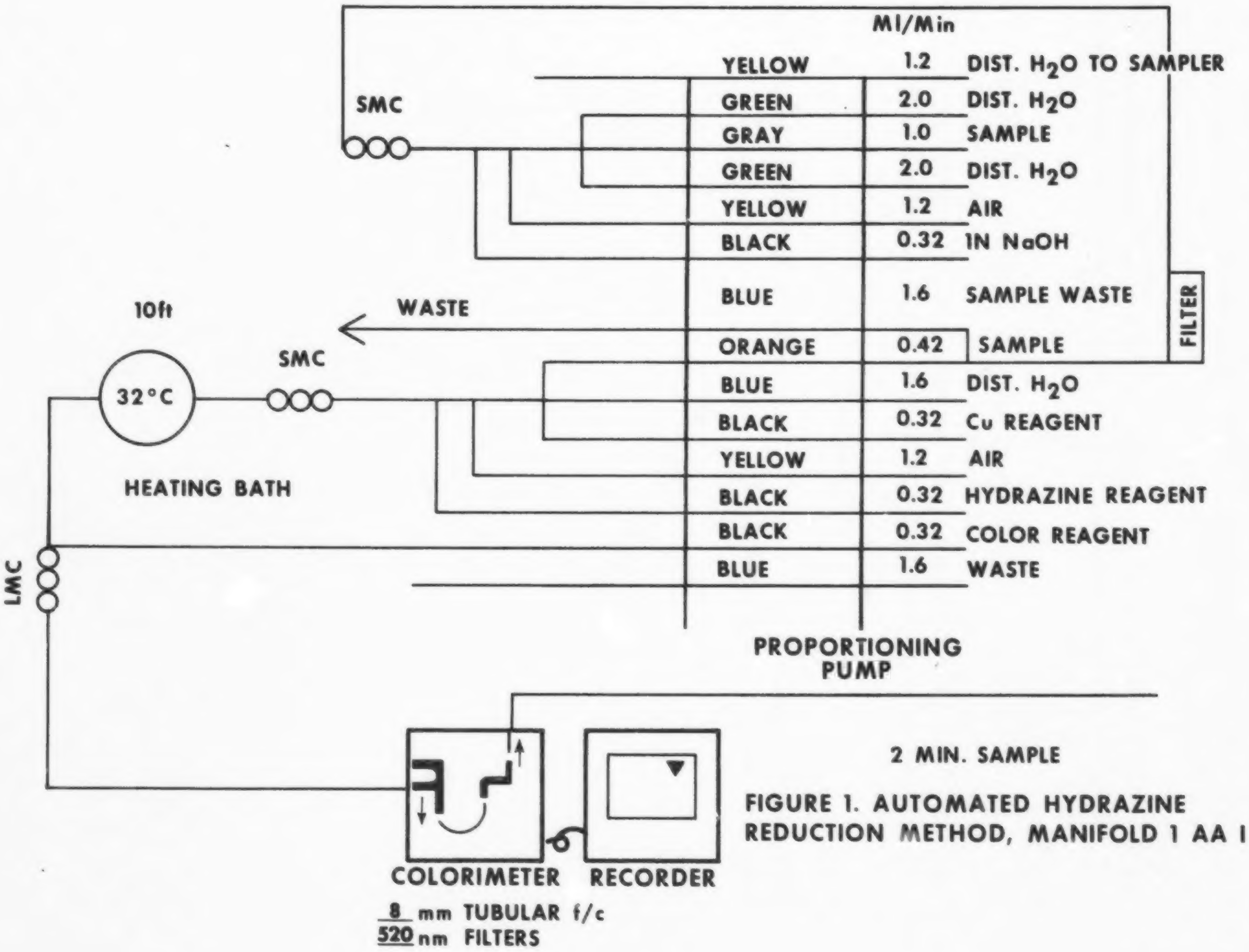
Ml/Min
YELLOW 1.2 DIST. H_2O TO SAMPLER
GREEN 2.0 DIST. H_2O
GRAY 1.0 SAMPLE
GREEN 2.0 DIST. H_2O
YELLOW 1.2 AIR
BLACK 0.32 1N NaOH
BLUE 1.6 SAMPLE WASTE
ORANGE 0.42 SAMPLE
BLUE 1.6 DIST. H_2O
BLACK 0.32 Cu REAGENT
YELLOW 1.2 AIR
BLACK 0.32 HYDRAZINE REAGENT
BLACK 0.32 COLOR REAGENT
BLUE 1.6 WASTE
FILTER
SMC
WASTE
SMC
10ft
32°C
HEATING BATH
LMC
PROPORTIONING PUMP
COLORIMETER
RECORDER
8 mm TUBULAR f/c
520 nm FILTERS
2 MIN. SAMPLE

FIGURE 1. AUTOMATED HYDRAZINE REDUCTION METHOD, MANIFOLD 1 AA I

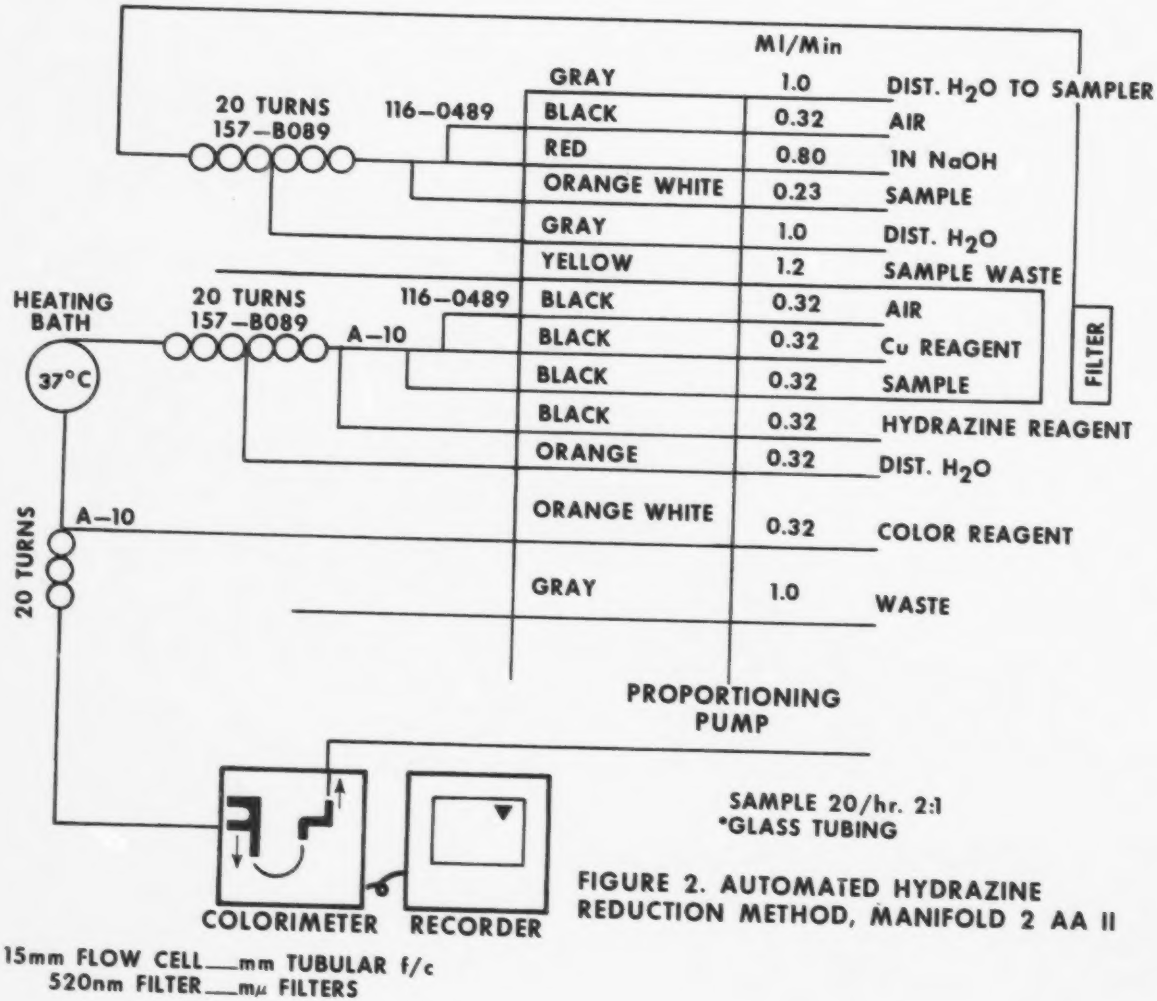
Ml/Min
GRAY 1.0 DIST. H_2O TO SAMPLER
BLACK 0.32 AIR
RED 0.80 1N NaOH
ORANGE WHITE 0.23 SAMPLE
GRAY 1.0 DIST. H_2O
YELLOW 1.2 SAMPLE WASTE
BLACK 0.32 AIR
BLACK 0.32 Cu REAGENT
BLACK 0.32 SAMPLE
BLACK 0.32 HYDRAZINE REAGENT
ORANGE 0.32 DIST. H_2O
ORANGE WHITE 0.32 COLOR REAGENT
GRAY 1.0 WASTE
FILTER
20 TURNS
157–B089
116–0489
20 TURNS
157–B089
116–0489
A–10
HEATING BATH
37°C
A–10
20 TURNS
PROPORTIONING PUMP
COLORIMETER
RECORDER
15mm FLOW CELL___mm TUBULAR f/c
520nm FILTER___mμ FILTERS
SAMPLE 20/hr. 2:1
•GLASS TUBING

FIGURE 2. AUTOMATED HYDRAZINE REDUCTION METHOD, MANIFOLD 2 AA II

NITROGEN, NITRATE-NITRITE

Method 353.2 (Colorimetric, Automated, Cadmium Reduction)

STORET NO. Total 00630

1. Scope and Application

   1.1 This method pertains to the determination of nitrite singly, or nitrite and nitrate combined in surface and saline waters, and domestic and industrial wastes. The applicable range of this method is 0.05 to 10.0 mg/1 nitrate-nitrite nitrogen. The range may be extended with sample dilution.

2. Summary of Method

   2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.

3. Sample Handling and Preservation

   3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml conc. H_2SO_4 per liter) and refrigeration.

   Caution: Samples for reduction column must not be preserved with mercuric chloride.

4. Interferences

   4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered.

   4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.

   4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.

5. Apparatus

   5.1 Technicon AutoAnalyzer (AAI or AAII) consisting of the following components:

      5.1.1 Sampler.
      5.1.2 Manifold (AAI) or analytical cartridge (AAII).
      5.1.3 Proportioning Pump
      5.1.4 Colorimeter equipped with a 15 mm or 50 mm tubular flow cell and 540 nm filters.
      5.1.5 Recorder.

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5.1.6 Digital printer for AAII (Optional).

6. Reagents

6.1 Granulated cadmium: 40-60 mesh (MCB Reagents).

6.2 Copper-cadmium: The cadmium granules (new or used) are cleaned with dilute HCl (6.7) and copperized with 2% solution of copper sulfate (6.8) in the following manner:

6.2.1 Wash the cadmium with HCl (6.7) and rinse with distilled water. The color of the cadmium so treated should be silver.

6.2.2 Swirl 10 g cadmium in 100 ml portions of 2% solution of copper sulfate (6.8) for five minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

6.2.3 Wash the cadmium-copper with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.

6.3 Preparation of reduction column AAI: The reduction column is an 8 by 50 mm glass tube with the ends reduced in diameter to permit insertion into the system. Copper-cadmium granules (6.2) are placed in the column between glass wool plugs. The packed reduction column is placed in an up-flow 20° incline to minimize channeling. See Figure 1.

6.4 Preparation of reduction column AAII: The reduction column is a U-shaped, 35 cm length, 2 mm I.D. glass tube (Note 1). Fill the reduction column with distilled water to prevent entrapment of air bubbles during the filling operations. Transfer the copper-cadmium granules (6.2) to the reduction column and place a glass wool plug in each end. To prevent entrapment of air bubbles in the reduction column be sure that all pump tubes are filled with reagents before putting the column into the analytical system.

NOTE 1: A 0.081 I.D. pump tube (purple) can be used in place of the 2 mm glass tube.

6.5 Distilled water: Because of possible contamination, this should be prepared by passage through an ion exchange column comprised of a mixture of both strongly acidic-cation and strongly basic-anion exchange resins. The regeneration of the ion exchange column should be carried out according to the manufacturer's instructions.

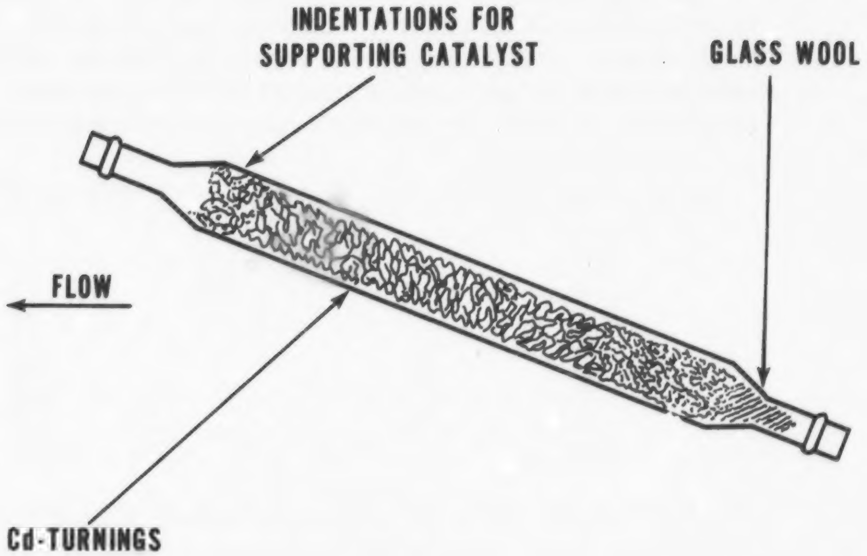
6.6 Color reagent: To approximately 800 ml of distilled water, add, while stirring, 100 ml conc. phosphoric acid, 40 g sulfanilamide, and 2 g N-1-naphthylethylenediamine dihydrochloride. Stir until dissolved and dilute to 1 liter. Store in brown bottle and keep in the dark when not in use. This solution is stable for several months.

6.7 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.

6.8 Copper sulfate solution, 2%: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 ml of distilled water and dilute to 1 liter.

6.9 Wash solution: Use distilled water for unpreserved samples. For samples preserved with H_2SO_4, use 2 ml H_2SO_4 per liter of wash water.

6.10 Ammonium chloride–EDTA solution: Dissolve 85 g of reagent grade ammonium chloride and 0.1 g of disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide and dilute to 1 liter. Add 1/2 ml Brij-35 (available from Technicon Corporation).


INDENTATIONS FOR
SUPPORTING CATALYST
GLASS WOOL
FLOW
Cd-TURNINGS

TILT COLUMN TO 20° POSTION

FIGURE 1. COPPER CADMIUM REDUCTION COLUMN
(1 1/2 ACTUAL SIZE)

6.11. Stock nitrate solution: Dissolve 7.218 g KNO_3 and dilute to 1 liter in a volumetric flask with distilled water. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months. 1 ml = 1.0 mg NO_3–N.

6.12 Stock nitrite solution: Dissolve 6.072 g KNO_2 in 500 ml of distilled water and dilute to 1 liter in a volumetric flask. Preserve with 2 ml of chloroform and keep under refrigeration. 1.0 ml = 1.0 mg NO_2–N.

6.13 Standard nitrate solution: Dilute 10.0 ml of stock nitrate solution (6.11) to 1000 ml. 1.0 ml = 0.01 mg NO_3-N. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months.

6.14 Standard nitrite solution: Dilute 10.0 ml of stock nitrite (6.12) solution to 1000 ml. 1.0 ml = 0.01 mg NO_2-N. Solution is unstable; prepare as required.

6.15 Using standard nitrate solution (6.13), prepare the following standards in 100.0 ml volumetric flasks. At least one nitrite standard should be compared to a nitrate standard at the same concentration to verify the efficiency of the reduction column.

Conc., mgNO_2–N or NO_3-N/l	ml Standard Solution/100 ml
0.0	0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0
2.00	20.0
4.00	40.0
6.00	60.0

NOTE 2: When the samples to be analyzed are saline waters, Substitute Ocean Water (SOW) should be used for preparing the standards; otherwise, distilled water is used. A tabulation of SOW composition follows:

NaCl – 24.53 g/l
$CaCl_2$ – 1.16 g/l
KBr – 0.10 g/l
NaF – 0.003 g/l
$MgCl_2$ – 5.20 g/l
KCl – 0.70 g/l
H_3BO_3 – 0.03 g/l
Na_2SO_4 – 4.09 g/l
$NaHCO_3$ – 0.20 g/l
$SrCl_2$ – 0.03 g/l

7. Procedure

7.1 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH_4OH.

7.2 Set up the manifold as shown in Figure 2 (AAI) or Figure 3 (AAII). Note that reductant column should be in 20° incline position (AAI). Care should be taken not to introduce air into reduction column on the AAII.

7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line.

NOTE 3: Condition column by running 1 mg/l standard for 10 minutes if a new reduction column is being used. Subsequently wash the column with reagents for 20 minutes.

7.4 Place appropriate nitrate and/or nitrite standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.5 For the AAI system, sample at a rate of 30/hr, 1:1. For the AAII, use a 40/hr, 4:1 cam and a common wash.

7.6 Switch sample line to sampler and start analysis.

8. Calculations

8.1 Prepare appropriate standard curve or curves derived from processing NO_2 and/or NO_3 standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 Three laboratories participating in an EPA Method Study, analyzed four natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrate Nitrogen mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.29	0.012	+ 5.75	+0.017
0.35	0.092	+18.10	+0.063
2.31	0.318	+ 4.47	+0.103
2.48	0.176	− 2.69	−0.067

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2. Armstrong, F. A., Stearns, C. R., and Strickland, J. D., "The Measurement of Upwelling and Subsequent Biological Processes by Means of the Technicon AutoAnalyzer and Associated Equipment", Deep Sea Research 14, p 381–389 (1967).
3. Annual Book of ASTM Standards, Part 31, "Water", Standard D1254, p 366 (1976).
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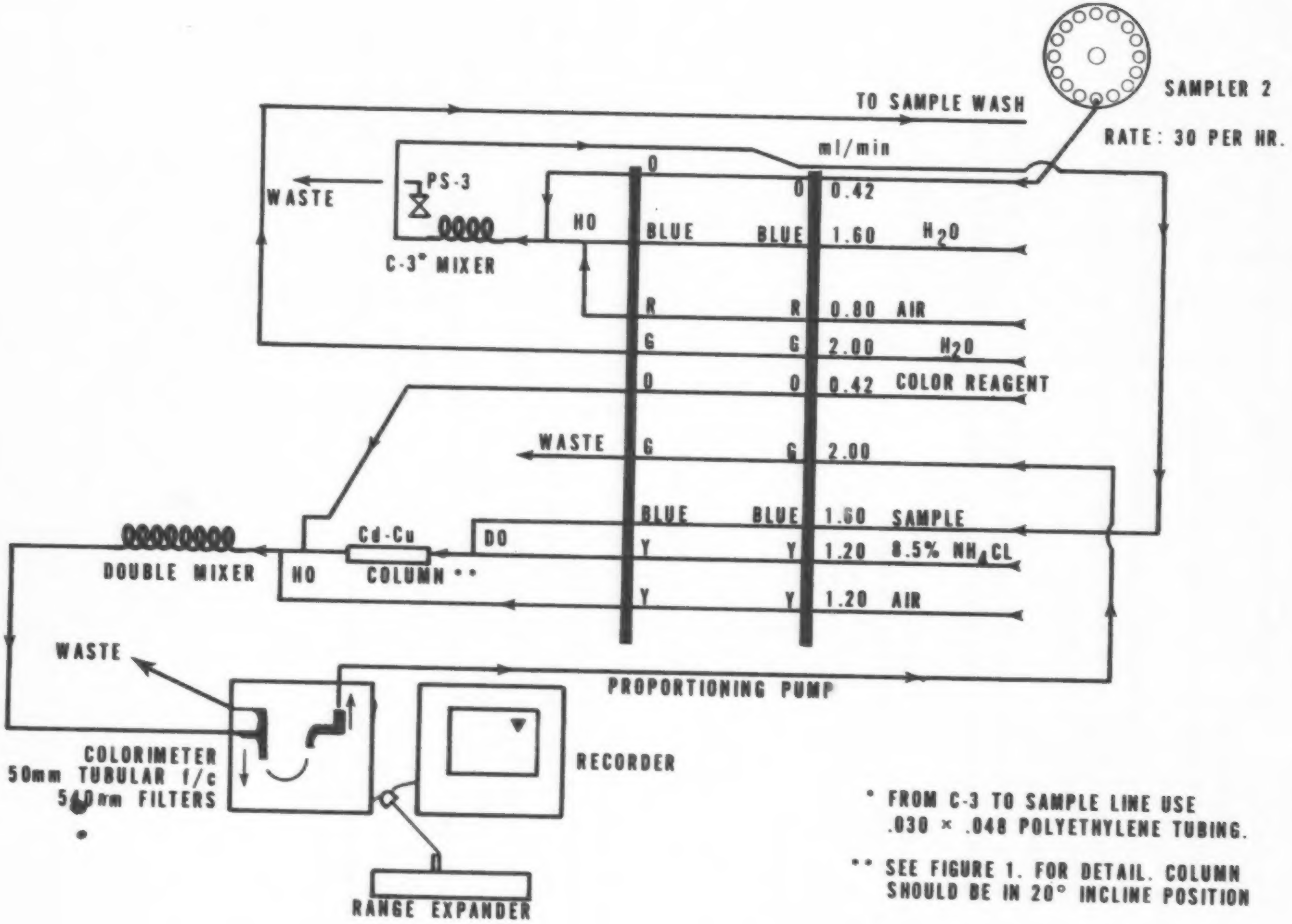
SAMPLER 2
RATE: 30 PER HR.
TO SAMPLE WASH
ml/min
WASTE
PS-3
C-3* MIXER
HO
O
O 0.42
BLUE
BLUE 1.60 H2O
R
R 0.80 AIR
G
G 2.00 H2O
O
O 0.42 COLOR REAGENT
WASTE
G
G 2.00
BLUE
BLUE 1.60 SAMPLE
Y
Y 1.20 8.5% NH4CL
Y
Y 1.20 AIR
DO
Cd-Cu
COLUMN **
HO
DOUBLE MIXER
WASTE
PROPORTIONING PUMP
COLORIMETER
50mm TUBULAR f/c
540nm FILTERS
RECORDER
RANGE EXPANDER

* FROM C-3 TO SAMPLE LINE USE .030 × .048 POLYETHYLENE TUBING.

** SEE FIGURE 1. FOR DETAIL. COLUMN SHOULD BE IN 20° INCLINE POSITION

FIGURE 2. NITRATE - NITRITE MANIFOLD AA-I

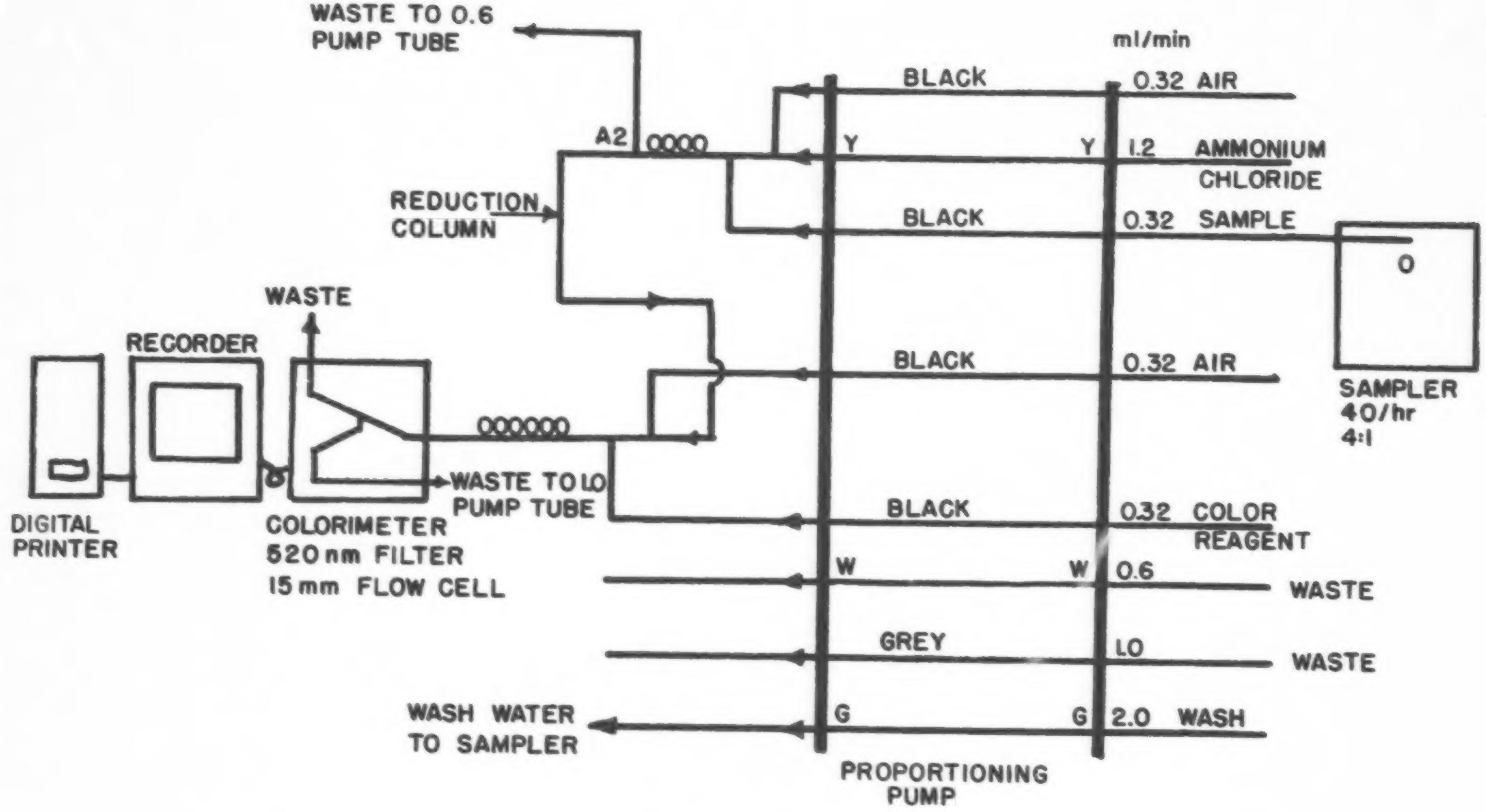
WASTE TO 0.6 PUMP TUBE
ml/min
BLACK
0.32 AIR
A2
Y
Y
1.2 AMMONIUM CHLORIDE
REDUCTION COLUMN
BLACK
0.32 SAMPLE
O
WASTE
RECORDER
BLACK
0.32 AIR
SAMPLER 40/hr 4:1
WASTE TO LO PUMP TUBE
BLACK
0.32 COLOR REAGENT
DIGITAL PRINTER
COLORIMETER 520 nm FILTER 15 mm FLOW CELL
W
W
0.6
WASTE
GREY
LO
WASTE
WASH WATER TO SAMPLER
G
G
2.0 WASH
PROPORTIONING PUMP

FIGURE 3 NITRATE-NITRITE MANIFOLD AA II

NITROGEN, NITRATE-NITRITE

Method 353.3 (Spectrophotometric, Cadmium Reduction)

STORET NO. Total 00630

1. Scope and Application
   1.1 This method is applicable to the determination of nitrite singly, or nitrite and nitrate combined in drinking, surface and saline waters, domestic and industrial wastes. The applicable range of this method is 0.01 to 1.0 mg/1 nitrate-nitrite nitrogen. The range may be extended with sample dilution.
2. Summary of Method
   2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N–(1-naphthyl)–ethylenediamine dihydrochloride to form a highly colored azo dye which is measured spectrophotometrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.
3. Sample Handling and Preservation
   3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml H_2SO_4 per liter) and refrigeration.
   Caution: Samples for reduction column must not be preserved with mercuric chloride.
4. Interferences
   4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered through a glass fiber filter or a 0.45*u* membrane filter. Highly turbid samples may be pretreated with zinc sulfate before filtration to remove the bulk of particulate matter present in the sample.
   4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.
   4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.
   4.4 This procedure determines both nitrate and nitrite. If only nitrate is desired, a separate determination must be made for nitrite and subsequent corrections made. The nitrite may be determined by the procedure below without the reduction step.

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5. Apparatus

5.1 Reduction column: The column in Figure I was constructed from a 100 ml pipet by removing the top portion. This column may also be constructed from two pieces of tubing joined end to end. A 10 mm length of 3 cm I.D. tubing is joined to a 25 cm length of 3.5 mm I.D. tubing.

5.2 Spectrophotometer for use at 540 nm, providing a light path of 1 cm or longer.

6. Reagents

6.1 Granulated cadmium: 40-60 mesh (MCB Reagents).

6.2 Copper-Cadmium: The cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate in the following manner:

6.2.1 Wash the cadmium with dilute HCl (6.10) and rinse with distilled water. The color of the cadmium should be silver.

6.2.2 Swirl 25 g cadmium in 100 ml portions of a 2% solution of copper sulfate (6.11) for 5 minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

6.2.3 Wash the copper-cadmium with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.

6.3 Preparation of reaction column: Insert a glass wool plug into the bottom of the reduction column and fill with distilled water. Add sufficient copper-cadmium granules to produce a column 18.5 cm in length. Maintain a level of distilled water above the copper-cadmium granules to eliminate entrapment of air. Wash the column with 200 ml of dilute ammonium chloride solution (6.5). The column is then activated by passing through the column 100 ml of a solution composed of 25 ml of a 1.0 mg/1 NO_3–N standard and 75 ml of ammonium chloride – EDTA solution (6.4). Use a flow rate between 7 and 10 ml per minute.

6.4 Ammonium chloride – EDTA solution: Dissolve 13 g ammonium chloride and 1.7 g disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide (6.9) and dilute to 1 liter.

6.5 Dilute ammonium chloride-EDTA solution: Dilute 300 ml of ammonium chloride-EDTA solution (6.4) to 500 ml with distilled water.

6.6 Color reagent: Dissolve 10 g sulfanilamide and 1 g N(1-naphthyl)–ethylene-diamine dihydrochloride in a mixture of 100 ml conc. phosphoric acid and 800 ml of distilled water and dilute to 1 liter with distilled water.

6.7 Zinc sulfate solution: Dissolve 100 g $ZnSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 liter.

6.8 Sodium hydroxide solution, 6N: Dissolve 240 g NaOH in 500 ml distilled water, cool and dilute to 1 liter.

6.9 Ammonium hydroxide, conc.

6.10 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.

6.11 Copper sulfate solution, 2%: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 ml of distilled water and dilute to 1 liter.

6.12 Stock nitrate solution: Dissolve 7.218 g KNO_3 in distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform per liter. This solution is stable for at least 6 months. 1.0 ml = 1.00 mg NO_3–N.

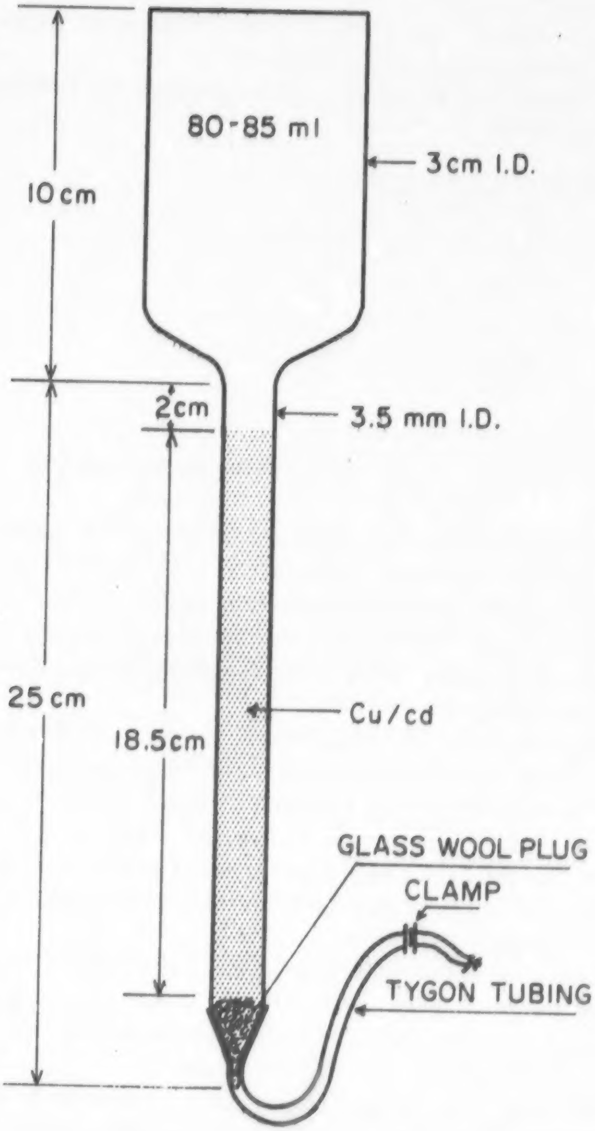
80-85 ml
3cm I.D.
10 cm
2cm
3.5 mm I.D.
25 cm
18.5cm
Cu/cd
GLASS WOOL PLUG
CLAMP
TYGON TUBING

FIGURE 1. REDUCTION COLUMN

6.13 Standard nitrate solution: Dilute 10.0 ml of nitrate stock solution (6.12) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO_3–N.

6.14 Stock nitrite solution: Dissolve 6.072 g KNO_2 in 500 ml of distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform and keep under refrigeration. Stable for approximately 3 months. 1.0 ml = 1.00 mg NO_2–N.

6.15 Standard nitrite solution: Dilute 10.0 ml of stock nitrite solution (6.14) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO_2–N.

6.16 Using standard nitrate solution (6.13) prepare the following standards in 100 ml volumetric flasks:

Conc., mg-NO_3–N/l	ml of Standard Solution/100.0 ml
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0

7. Procedure

7.1 Turbidity removal: One of the following methods may be used to remove suspended matter.

7.1.1 Filter sample through a glass fiber filter or a 0.45*u* membrane filter.

7.1.2 Add 1 ml zinc sulfate solution (6.7) to 100 ml of sample and mix thoroughly. Add 0.4–0.5 ml sodium hydroxide solution (6.8) to obtain a pH of 10.5 as determined with a pH meter. Let the treated sample stand a few minutes to allow the heavy flocculent precipitate to settle. Clarify by filtering through a glass fiber filter or a 0.45*u* membrane filter.

7.2 Oil and grease removal: Adjust the pH of 100 ml of filtered sample to 2 by addition of conc. HCl. Extract the oil and grease from the aqueous solution with two 25 ml portions of a non-polar solvent (Freon, chloroform or equivalent).

7.3 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH_4OH. This is done to insure a sample pH of 8.5 after step 7.4.

7.4 To 25.0 ml of sample or an aliquot diluted to 25.0 ml, add 75 ml of ammonium chloride-EDTA solution (6.4) and mix.

7.5 Pour sample into column and collect sample at a rate of 7–10 ml per minute.

7.6 Discard the first 25 ml, collect the rest of the sample (approximately 70 ml) in the original sample flask. Reduced samples should not be allowed to stand longer than 15 minutes before addition of color reagent, step 7.7.

7.7 Add 2.0 ml of color reagent (6.6) to 50.0 ml of sample. Allow 10 minutes for color development. Within 2 hours measure the absorbance at 540 nm against a reagent blank. **NOTE:** If the concentration of sample exceeds 1.0 mg NO_3–N/1, the remainder of the reduced sample may be used to make an appropriate dilution before proceeding with step 7.7.

7.8 Standards: Carry out the reduction of standards exactly as described for the samples. At least one nitrite standard should be compared to a reduced nitrate standard at the same concentration to verify the efficiency of the reduction column.

8. Calculation

8.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against NO_3–N mg/1. Compute concentration of samples by comparing sample absorbance with standard curve.

8.2 If less than 25 ml of sample is used for the analysis the following equation should be used:

$$\text{mg}NO_2 + NO_3 - N/1 = \frac{A \times 25}{\text{ml sample used}}$$

where:

A = Concentration of nitrate from standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using sewage samples at concentrations of 0.04, 0.24, 0.55 and 1.04 mg $NO_3 + NO_2$-N/1, the standard deviations were ±0.005, ±0.004, ±0.005 and ±0.01, respectively.

9.2 In a single laboratory (EMSL), using sewage samples at concentrations of 0.24, 0.55, and 1.05 mg $NO_3 + NO_2$–N/1, the recoveries were 100%, 102% and 100%, respectively.

Bibliography

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3. Grasshoff, K., "A Simultaneous Multiple Channel System for Nutrient Analysis in Sea Water with Analog and Digital Data Record", "Advances in Automated Analysis", Technicon International Congress, 1969, Vol. 11, p 133–145.
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NITROGEN, NITRITE

Method 354.1 (Spectrophotometric)

STORET NO. Total 00615

1. Scope and Application
   - 1.1 This method is applicable to the determination of nitrite in drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 The method is applicable in the range from 0.01 to 1.0 mg NO_2–N/1.
2. Summary of Method
   - 2.1 The diazonium compound formed by diazotation of sulfanilamide by nitrite in water under acid conditions is coupled with N–(1-naphthyl)–ethylenediamine dihydrochloride to produce a reddish-purple color which is read in a spectrophotometer at 540 nm.
3. Sample Handling and Preservation
   - 3.1 Samples should be analyzed as soon as possible. They may be stored for 24 to 48 hours at 4°C.
4. Interferences
   - 4.1 There are very few known interferences at concentrations less than 1,000 times that of the nitrite; however, the presence of strong oxidants or reductants in the samples will readily affect the nitrite concentrations. High alkalinity ($>$600 mg/1) will give low results due to a shift in pH.
5. Apparatus
   - 5.1 Spectrophotometer equipped with 1 cm or larger cells for use at 540 nm.
   - 5.2 Nessler tubes, 50 ml or volumetric flasks, 50 ml.
6. Reagents
   - 6.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.
   - 6.2 Buffer-color reagent: To 250 ml of distilled water, add 105 ml conc. hydrochloric acid, 5.0 g sulfanilamide and 0.5 g N–(1-naphthyl) ethylenediamine dihydrochloride. Stir until dissolved. Add 136 g of sodium acetate ($CH_3COONa \cdot 3H_2O$) and again stir until dissolved. Dilute to 500 ml with distilled water. This solution is stable for several weeks if stored in the dark.
   - 6.3 Nitrite stock solution: 1.0 ml = 0.10 mg NO_2–N. Dissolve 0.1493 g of dried anhydrous sodium nitrite (24 hours in desiccator) in distilled water and dilute to 1000 ml. Preserve with 2 ml chloroform per liter.
   - 6.4 Nitrite standard solution: 1.0 ml = 0.001 mg NO_2–N. Dilute 10.0 ml of the stock solution (6.3) to 1000 ml.
7. Procedure
   - 7.1 If the sample has a pH greater than 10 or a total alkalinity in excess of 600 mg/1, adjust to approximately pH 6 with 1:3 HCl.

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7.2 If necessary, filter the sample through a 0.45 *u* pore size filter using the first portion of filtrate to rinse the filter flask.

7.3 Place 50 ml of sample, or an aliquot diluted to 50 ml, in a 50 ml Nessler tube; hold until preparation of standards is completed.

7.4 At the same time prepare a series of standards in 50 ml Nessler tubes as follows:

ml of Standard Solution 1.0 ml = 0.001 mg NO_2-N	Conc., When Diluted to 50 ml, mg/l of NO_2–N
0.0	(Blank)
0.5	0.01
1.0	0.02
1.5	0.03
2.0	0.04
3.0	0.06
4.0	0.08
5.0	0.10
10.0	0.20

7.5 Add 2 ml of buffer-color reagent (6.2) to each standard and sample, mix and allow color to develop for at least 15 minutes. The color reaction medium should be between pH 1.5 and 2.0.

7.6 Read the color in the spectrophotometer at 540 nm against the blank and plot concentration of NO_2–N against absorbance.

8. Calculation

8.1 Read the concentration of NO_2–N directly from the curve.

8.2 If less than 50.0 ml of sample is taken, calculate mg/1 as follows:

$$NO_2 - N, \text{mg/l} = \frac{\text{mg/l from std. curve} \times 50}{\text{ml sample used}}$$

9. Precision and Accuracy

9.1 Precision and Accuracy data are not available at this time.

Bibliography

1. Standard Methods for the Examination for Water and Wastewater, 14th Edition, p 434, Method 420, (1975).

OXYGEN, DISSOLVED

Method 360.1 (Membrane Electrode)

STORET NO. 00299

1. Scope and Application

   1.1 The probe method for dissolved oxygen is recommended for those samples containing materials which interfere with the modified Winkler procedure such as sulfite, thiosulfate, polythionate, mercaptans, free chlorine or hypochlorite, organic substances readily hydrolyzed in alkaline solutions, free iodine, intense color or turbidity and biological flocs.

   1.2 The probe method is recommended as a substitute for the modified Winkler procedure in monitoring of streams, lakes, outfalls, etc., where it is desired to obtain a continuous record of the dissolved oxygen content of the water under observation.

   1.3 The probe method may be used as a substitute for the modified Winkler procedure in **BOD** determinations where it is desired to perform nondestructive DO measurements on a sample.

   1.4 The probe method may be used under any circumstances as a substitute for the modified Winkler procedure provided that the probe itself is standardized against the Winkler method on samples free of interfering materials.

   1.5 The electronic readout meter for the output from dissolved oxygen probes is normally calibrated in convenient scale (0 to 10, 0 to 15, 0 to 20 mg/1 for example) with a sensitivity of approximately 0.05 mg/liter.

2. Summary of Method

   2.1 The most common instrumental probes for determination of dissolved oxygen in water are dependent upon electrochemical reactions. Under steady-state conditions, the current or potential can be correlated with DO concentrations. Interfacial dynamics at the probe-sample interface are a factor in probe response and a significant degree of interfacial turbulence is necessary. For precision performance, turbulence should be constant.

3. Sample Handling and Preservation

   3.1 See 4.1, 4.2, 4.3, 4.4 under Modified Winkler Method (360.2).

4. Interferences

   4.1 Dissolved organic materials are not known to interfere in the output from dissolved oxygen probes.

   4.2 Dissolved inorganic salts are a factor in the performance of dissolved oxygen probe.

   4.2.1 Probes with membranes respond to partial pressure of oxygen which in turn is a function of dissolved inorganic salts. Conversion factors for seawater and brackish waters may be calculated from dissolved oxygen saturation versus salinity data. Conversion factors for specific inorganic salts may be developed experimentally.

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Broad variations in the kinds and concentrations of salts in samples can make the use of a membrane probe difficult.

4.3 Reactive compounds can interfere with the output or the performance of dissolved oxygen probes.

4.3.1 Reactive gases which pass through the membrane probes may interfere. For example, chlorine will depolarize the cathode and cause a high probe-output. Long-term exposures to chlorine will coat the anode with the chloride of the anode metal and eventually desensitize the probe. Alkaline samples in which free chlorine does not exist will not interfere. Hydrogen sulfide will interfere with membrane probes if the applied potential is greater than the half-wave potential of the sulfide ion. If the applied potential is less than the half-wave potential, an interfering reaction will not occur, but coating of the anode with the sulfide of the anode metal can take place.

4.4 Dissolved oxygen probes are temperature sensitive, and temperature compensation is normally provided by the manufacturer. Membrane probes have a temperature coefficient of 4 to 6 percent/°C dependent upon the membrane employed.

5. Apparatus

5.1 No specific probe or accessory is especially recommended as superior. However, probes which have been evaluated or are in use and found to be reliable are the Weston & Stack DO Analyzer Model 30, the Yellow Springs Instrument (YSI) Model 54, and the Beckman Fieldlab Oxygen Analyzer.

6. Calibration

Follow manufacturer instructions.

7. Procedure

Follow manufacturer instructions.

8. Calculation

Follow manufacturer instructions.

9. Precision and Accuracy

Manufacturer's specification claim 0.1 mg/1 repeatability with ±1% accuracy.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 450, Method 422F (1975).

OXYGEN, DISSOLVED

Method 360.2 (Modified Winkler, Full-Bottle Technique)

STORET NO. 00300

1. Scope and Application
    1.1 This method is applicable for use with most wastewaters and streams that contain nitrate nitrogen and not more than 1 mg/l of ferrous iron. Other reducing or oxidizing materials should be absent. If 1 ml of fluoride solution is added before acidifying the sample and there is no delay in titration, the method is also applicable in the presence of 100–200 mg/l ferric iron.
    1.2 The Dissolved Oxygen (DO) Probe technique gives comparable results on all samples types.
    1.3 The azide modification is not applicable under the following conditions: (a) samples containing sulfite, thiosulfate, polythionate, appreciable quantities of free chlorine or hypochlorite; (b) samples high in suspended solids; (c) samples containing organic substances which are readily oxidized in a highly alkaline solution, or which are oxidized by free iodine in an acid solution; (d) untreated domestic sewage; (e) biological flocs; and (f) where sample color interferes with endpoint detection. In instances where the azide modification is not applicable, the DO probe should be used.
2. Summary of Method
    2.1 The sample is treated with manganous sulfate, potassium hydroxide, and potassium iodide (the latter two reagents combined in one solution) and finally sulfuric acid. The initial precipitate of manganous hydroxide, $Mn(OH)_2$, combines with the dissolved oxygen in the sample to form a brown precipitate, manganic hydroxide, $MnO(OH)_2$. Upon acidification, the manganic hydroxide forms manganic sulfate which acts as an oxidizing agent to release free iodine from the potassium iodide. The iodine, which is stoichiometrically equivalent to the dissolved oxygen in the sample is then titrated with sodium thiosulfate or phenylarsine oxide (PAO).
3. Interferences
    3.1 There are a number of interferences to the dissolved oxygen test, including oxidizing and reducing agents, nitrate ion, ferrous iron, and organic matter.
    3.2 Various modifications of the original Winkler procedure for dissolved oxygen have been developed to compensate for or eliminate interferences. The Alsterberg modification is commonly used to successfully eliminate the nitrite interference, the Rideal-Stewart modification is designed to eliminate ferrous iron interference, and the Theriault procedure is used to compensate for high concentration of organic materials.
    3.3 Most of the common interferences in the Winkler procedure may be overcome by use of the dissolved oxygen probe.

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4. Sample Handling and Preservation

4.1 Where possible, collect the sample in a **300 ml BOD** incubation bottle. Special precautions are required to avoid entrainment or solution of atmospheric oxygen or loss of dissolved oxygen.

4.2 Where samples are collected from shallow depths (less than 5 feet), use of an APHA-type sampler is recommended. Use of a Kemmerer type sampler is recommended for samples collected from depths of greater than 5 feet.

4.3 When a Kemmerer sampler is used, the **BOD** sample bottle should be filled to overflowing. (overflow for approximately 10 seconds). Outlet tube of Kemmerer should be inserted to bottom of **BOD** bottle. Care must be taken to prevent turbulence and the formation of bubbles when filling bottle.

4.4 At time of sampling, the sample temperature should be recorded as precisely as required.

4.5 Do not delay the determination of dissolved oxygen in samples having an appreciable iodine demand or containing ferrous iron. If samples must be preserved either method (4.5.1) or (4.5.2) below, may be employed.

4.5.1 Add 2 ml of manganous sulfate solution (6.1) and then 2 ml of alkaline iodide-azide solution (6.2) to the sample contained in the **BOD** bottle. Both reagents must be added well below the surface of the liquid. Stopper the bottle immediately and mix the contents thoroughly. The sample should be stored at the temperature of the collection water, or water sealed and kept at a temperature of 10 to 20°C, in the dark. Complete the procedure by adding 2 ml H_2SO_4 (see 7.1) at time of analysis.

4.5.2 Add 0.7 ml of conc. H_2SO_4 (6.3) and 1 ml sodium azide solution (2 g NaN_3 in 100 ml distilled water) to sample in the **BOD** bottle. Store sample as in (4.5.1). Complete the procedure using 2 ml of manganous sulfate solution (6.1), 3 ml alkaline iodide-azide solution (6.2), and 2 ml of conc. H_2SO_4 (6.3) at time of analysis.

4.6 If either preservation technique is employed, complete the analysis within 4–8 hours after sampling.

5. Apparatus

5.1 Sample bottles-300 ml ±3 ml capacity **BOD** incubation bottles with tapered ground glass pointed stoppers and flared mouths.

5.2 Pipets-with elongated tips capable of delivering 2.0 ml ±0.10 ml of reagent.

6. Reagents

6.1 Manganous sulfate solution: Dissolve 480 g manganous sulfate ($MnSO_4 \cdot 4H_2O$ in distilled water and dilute to 1 liter.

6.1.1 Alternatively, use 400 g of $MnSO_4 \cdot 2H_2O$ or 364 g of $MnSO_4 \cdot H_2O$ per liter. When uncertainty exists regarding the water of crystallization, a solution of equivalent strength may be obtained by adjusting the specific gravity of the solution to 1.270 at 20°C.

6.2 Alkaline iodide-azide solution: Dissolve 500 g of sodium hydroxide ($NaOH$) or 700 g of potassium hydroxide (KOH) and 135 g of sodium iodide (NaI) or 150 g of potassium iodide (KI) in distilled water and dilute to 1 liter. To this solution add 10 g of solution azide (NaN_3) dissolved in 40 ml of distilled water.

6.3 Sulfuric acid: concentrated.

6.4 Starch solution: Prepare an emulsion of 10 g soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator.

6.4.1 Dry, powdered starch indicators such as "thyodene" may be used in place of starch solution.

6.5 Potassium fluoride solution: Dissolve 40 g $KF \cdot 2H_2O$ in distilled water and dilute to 100 ml.

6.6 Sodium thiosulfate, stock solution, 0.75 N: Dissolve 186.15 g $Na_2S_2O_3 \cdot 5H_2O$ in boiled and cooled distilled water and dilute to 1 liter. Preserve by adding 5 ml chloroform.

6.7 Sodium thiosulfate standard titrant, 0.0375 N: Prepare by diluting 50.0 ml of stock solution to 1 liter. Preserve by adding 5 ml of chloroform. Standard sodium thiosulfate, exactly 0.0375 N is equivalent to 0.300 mg of DO per 1.00 ml. Standardize with 0.0375 N potassium biiodate.

6.8 Potassium biiodate standard, 0.0375 N: For stock solution, dissolve 4.873 g of potassium biiodate, previously dried 2 hours at 103°C, in 1000 ml of distilled water. To prepare working standard, dilute 250 ml to 1000 ml for 0.0375 N biiodate solution.

6.9 Standardization of 0.0375 N sodium thiosulfate: Dissolve approximately 2 g (±1.0 g) KI in 100 to 150 ml distilled water; add 10 ml of 10% H_2SO_4 followed by 20.0 ml standard potassium biiodate (6.8). Place in dark for 5 minutes, dilute to 300 ml, and titrate with the standard sodium thiosulfate (6.7) to a pale straw color. Add 1–2 ml starch solution and continue the titration drop by drop until the blue color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

6.10 As an alternative to the sodium thiosulfate, phenylarsine oxide (**PAO**) may be used. This is available, already standardized, from commercial sources.

7. Procedure

7.1 To the sample collected in the **BOD** incubation bottle, add 2 ml of the manganous sulfate solution (6.1) followed by 2 ml of the alkaline iodide-azide solution (6.2), well below the surface of the liquid; stopper with care to exclude air bubbles, and mix well by inverting the bottle several times. When the precipitate settles, leaving a clear supernatant above the manganese hydroxide floc, shake again. When settling has produced at least 200 ml of clear supernatant, carefully remove the stopper and immediately add 2 ml of conc. H_2SO_4 (6.3) (sulfamic acid packets, 3 g may be substituted for H_2SO_4)(1) by allowing the acid to run down the neck of the bottle, re-stopper, and mix by gentle inversion until the iodine is uniformly distributed throughout the bottle. Complete the analysis within 45 minutes.

7.2 Transfer the entire bottle contents by inversion into a 500 ml wide mouth flask and titrate with 0.0375 N thiosulfate solution (6.7) (0.0375 N phenyarsine oxide (**PAO**) may be substituted as titrant) to pale straw color. Add 1–2 ml of starch solution (6.4) or 0.1 g of powdered indicator and continue to titrate to the first disappearance of the blue color.

7.3 If ferric iron is present (100 to 200 mg/1), add 1.0 ml of KF (6.5) solution before acidification.

7.4 Occasionally, a dark brown or black precipitate persists in the bottle after acidication. This precipitate will dissolve if the solution is kept for a few minutes longer than usual or, if particularly persistent, a few more drops of H_2SO_4 will effect dissolution.

8. Calculation

8.1 Each ml of 0.0375N sodium thiosulfate (or PAO) titrant is equivalent to 1 mg DO when the entire bottle contents are titrated.

8.2 If the results are desired in milliliters of oxygen gas per liter at 0°C and 760 mm pressure multiply mg/1 DO by 0.698.

8.3 To express the results as percent saturation at 760 mm atmospheric pressure, the solubility data in Table 422:1 (Whipple & Whipple, p 446–447, Standard Methods, 14th Edition) may be used. Equations for correcting the solubilities to barometric pressures other than mean sea level are given below the table.

8.4 The solubility of DO in distilled water at any barometric pressure, p (mm Hg), temperature, T°C, and saturated vapor pressure, *u* (mm Hg), for the given T, may be calculated between the temperature of 0° and 30°C by:

$$\text{ml/l DO} = \frac{(P - u) \times 0.678}{35 + T}$$

and between 30° and 50°C by:

$$\text{ml/l DO} = \frac{(P - u) \times 0.827}{49 + T}$$

9. Precision and Accuracy

9.1 Exact data are unavailable on the precision and accuracy of this technique; however, reproducibility is approximately 0.2 mg/1 of DO at the 7.5 mg/1 level due to equipment tolerances and uncompensated displacement errors.

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PHOSPHORUS, ALL FORMS

Method 365.1 (Colorimetric, Automated, Ascorbic Acid)

STORET NO. See Section 4

1. Scope and Application
   1.1 These methods cover the determination of specified forms of phosphorus in drinking, surface and saline waters, domestic and industrial wastes.
   1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are defined in Section 4.
      1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples. Insoluble forms of phosphorus are determined by calculation.
   1.3 The methods are usable in the 0.01 to 1.0 mg P/l range. Approximately 20-30 samples per hour can be analyzed.
2. Summary of Method
   2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.
   2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by manual sulfuric acid hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by manual persulfate digestion(2). The developed color is measured automatically on the AutoAnalyzer.
3. Sample Handling and Preservation
   3.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.
   3.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.
   3.3 If the analysis cannot be performed the same day of collection, the sample should be preserved by the addition of 2 ml conc. H_2SO_4 per liter and refrigeration at 4°C.
4. Definitions and Storet Numbers
   4.1 Total Phosphorus (P) – all of the phosphorus present in the sample regardless of form, as measured by the persulfate digestion procedure. (00665)
      4.1.1 Total Orthophosphate (P-ortho)–inorganic phosphorus $[(PO_4)^{-3}]$ in the sample as measured by the direct colorimetric analysis procedure. (70507)

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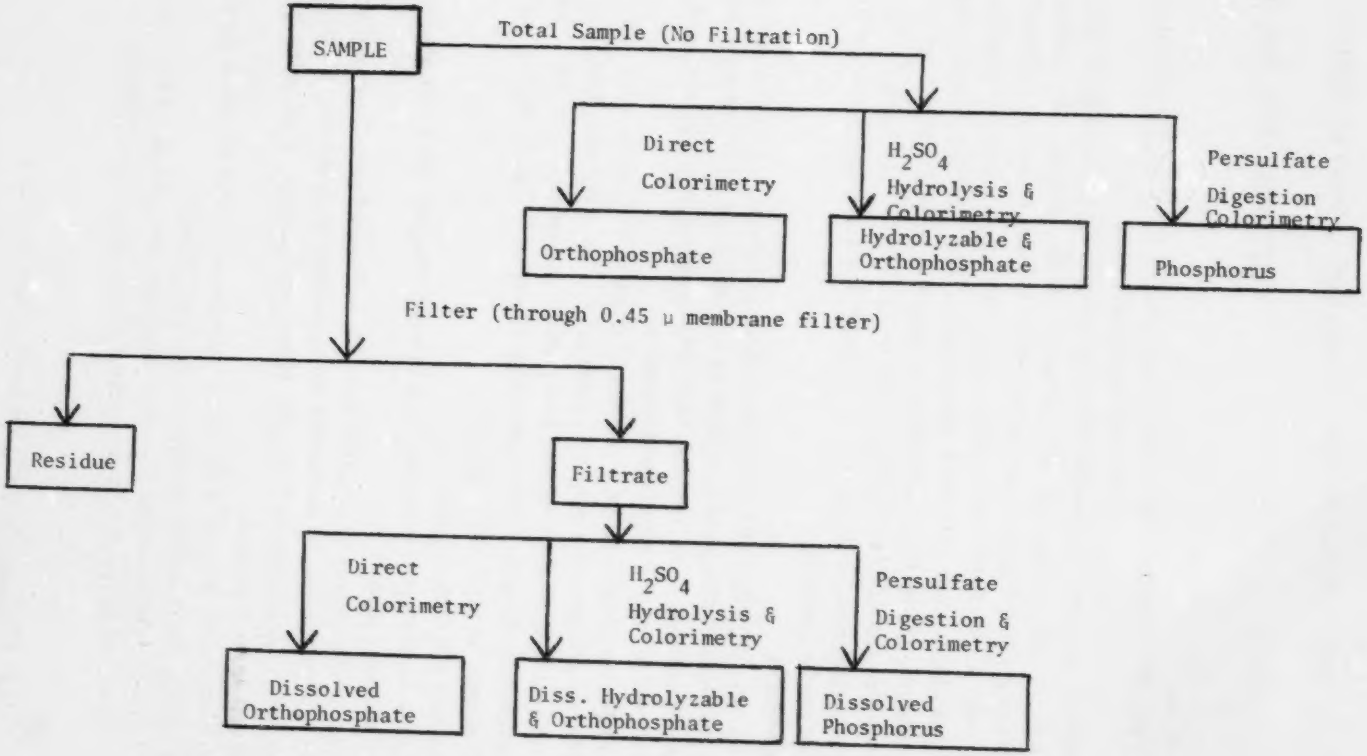
SAMPLE
Total Sample (No Filtration)
Direct
Colorimetry
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Hydrolyzable &
Orthophosphate
Persulfate
Digestion
Colorimetry
Phosphorus
Filter (through 0.45 μ membrane filter)
Residue
Filtrate
Direct
Colorimetry
Dissolved
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Diss. Hydrolyzable
& Orthophosphate
Persulfate
Digestion &
Colorimetry
Dissolved
Phosphorus

FIGURE 1. ANALYTICAL SCHEME FOR DIFFERENTIATION OF PHOSPHORUS FORMS

4.1.2 Total Hydrolyzable Phosphorus (P-hydro)–phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus predetermined orthophosphates. This hydrolyzable phosphorus includes polyphosphates $[(P_2O_7)^{-4}, (P_3O_{10})^{-5}$, etc.] plus some organic phosphorus. (00669)

4.1.3 Total Organic Phosphorus (P-org)–phosphorus (inorganic plus oxidizable organic) in the sample as measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)

4.2 Dissolved Phosphorus (P–D) – all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)

4.2.1 Dissolved Orthophosphate (P–D, ortho) – as measured by the direct colorimetric analysis procedure. (00671)

4.2.2 Dissolved Hydrolyzable Phosphorus (P–D, hydro) – as measured by the sulfuric acid hydrolysis procedure and minus predetermined dissolved orthophosphates. (00672)

4.2.3 Dissolved Organic Phosphorus (P–D, org) – as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)

4.3 The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

4.3.1 Insoluble Phosphorus (P–I)=(P) – (P–D). (00667)

4.3.1.1 Insoluble orthophosphate (P–I, ortho)=(P, ortho) – (P–D, ortho). (00674)

4.3.1.2 Insoluble Hydrolyzable Phosphorus (P–I, hydro) = (P, hydro) – (P–D, hydro). (00675)

4.3.1.3 Insoluble Organic Phosphorus (P–I, org) = (P, org) – (P–D, org). (00676)

4.4 All phosphorus forms shall be reported as P, mg/1, to the third place.

5. Interferences

5.1 No interference is caused by copper, iron, or silicate at concentrations many times greater than their reported concentration in sea water. However, high iron concentrations can cause precipitation of and subsequent loss of phosphorus.

5.2 The salt error for samples ranging from 5 to 20% salt content was found to be less than 1%.

5.3 Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus. However, at concentrations found in sea water, it does not interfere.

5.4 Sample turbidity must be removed by filtration prior to analysis for orthophosphate. Samples for total or total hydrolyzable phosphorus should be filtered only after digestion. Sample color that absorbs in the photometric range used for analysis will also interfere.

6. Apparatus

6.1 Technicon AutoAnalyzer consisting of:

6.1.1 Sampler.

6.1.2 Manifold (AAI) or Analytical Cartridge (AAII).

6.1.3 Proportioning pump.

6.1.4 Heating bath, 50°C.

6.1.5 Colorimeter equipped with 15 or 50 mm tubular flow cell.

6.1.6 650–660 or 880 nm filter.

6.1.7 Recorder.

6.1.8 Digital printer for AAII (optional).

6.2 Hot plate or autoclave.

6.3 Acid-washed glassware: All glassware used in the determination should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergent should never be used.

7. Reagents

7.1 Sulfuric acid solution, 5N: Slowly add 70 ml of conc. H_2SO_4 to approximately 400 ml of distilled water. Cool to room temperature and dilute to 500 ml with distilled water.

7.2 Antimony potassium tartrate solution: Weigh 0.3 g $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$, dissolve in 50 ml distilled water in 100 ml volumetric flask, dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 4 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 100 ml distilled water. Store in a plastic bottle at 4°C.

7.4 Ascorbic acid, 0.1M: Dissolve 1.8 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if prepared with water containing no more than trace amounts of heavy metals and stored at 4°C.

7.5 Combined reagent (AAI): Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N H_2SO_4 (7.1), 5 ml of antimony potassium tartrate solution (7.2), 15 ml of ammonium molybdate solution (7.3), and 30 ml of ascorbic acid solution (7.4). Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until the turbidity disappears before processing. This volume is sufficient for 4 hours operation. Since the stability of this solution is limited, it must be freshly prepared for each run.

NOTE 1: A stable solution can be prepared by not including the ascorbic acid in the combined reagent. If this is done, the mixed reagent (molybdate, tartrate, and acid) is pumped through the distilled water line and the ascorbic acid solution (30 ml of 7.4 diluted to 100 ml with distilled water) through the original mixed reagent line.

7.6 Sulfuric acid solution, 11 N: Slowly add 310 ml conc. H_2SO_4 to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Acid wash water: Add 40 ml of sulfuric acid solution (7.6) to 1 liter of distilled water and dilute to 2 liters. (Not to be used when only orthophosphate is being determined).

7.9 Phenolphthalein indicator solution (5 g/1): Dissolve 0.5 g of phenolphthalein in a solution of 50 ml of ethyl or isopropyl alcohol and 50 ml of distilled water.

7.10 Stock phosphorus solution: Dissolve 0.4393 g of pre-dried (105°C for 1 hour) KH_2PO_4 in distilled water and dilute to 1000 ml. 1.0 ml = 0.1 mg P.

7.11 Standard phosphorus solution: Dilute 100.0 ml of stock solution (7.10) to 1000 ml with distilled water. 1.0 ml = 0.01 mg P.

7.12 Standard phosphorus solution: Dilute 100.0 ml of standard solution (7.11) to 1000 ml with distilled water. 1.0 ml = 0.001 mg P.

7.13 Prepare a series of standards by diluting suitable volumes of standard solutions (7.11) and (7.12) to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Standard Phosphorus Solution (7.12)	Conc., mg P/l
0.0	0.00
2.0	0.02
5.0	0.05
10.0	0.10

ml of Standard Phosphorus Solution (7.11)	mg P/1
2.0	0.20
5.0	0.50
8.0	0.80
10.0	1.00

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of sulfuric acid solution (7.6) to a 50 ml sample and/or standard in a 125 ml Erlenmeyer flask.

8.1.2 Add 0.4 g of ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30–40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternately, heat for 30 minutes in an autoclave at 121°C (15–20 psi).

8.1.4 Cool and dilute the sample to 50 ml. If sample is not clear at this point, filter.

8.1.5 Determine phosphorus as outlined in (8.3.2) with acid wash water (7.8) in wash tubes.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of sulfuric acid solution (7.6) to a 50 ml sample and/or standard in a 125 ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for 30–40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15–20 psi).

8.2.3 Cool and dilute the sample to 50 ml. If sample is not clear at this point, filter.

8.2.4 Determine phosphorus as outlined in (8.3.2) with acid wash water (7.8) in wash tubes.

8.3 Orthophosphate

8.3.1 Add 1 drop of phenolphthalein indicator solution (7.9) to approximately 50 ml of sample. If a red color develops, add sulfuric acid solution (7.6) drop-wise to just discharge the color. Acid samples must be neutralized with 1 N sodium hydroxide (40 g NaOH/1).

8.3.2 Set up manifold as shown in Figure 2, AAI or Figure 3, AAII.

8.3.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line.

8.3.4 For the AAI system, sample at a rate of 20/hr, 1 minute sample, 2 minute wash. For the AAII system, use a 30/hr, 2:1 cam, and a common wash.

8.3.5 Place standards in Sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

8.3.6 Switch sample line from distilled water to Sampler and begin analysis.

9. Calculation

9.1 Prepare a standard curve by plotting peak heights of processed standards against known concentrations. Compute concentrations of samples by comparing sample peak heights with standard curve. Any sample whose computed value is less than 5% of its immediate predecessor must be rerun.

10. Precision and Accuracy (AAI system)

10.1 Six laboratories participating in an EPA Method Study, analyzed four natural water samples containing exact increments of orthophosphate, with the following results:

Increment as Orthophosphate mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as	
		Bias, %	Bias, mg P/liter
0.04	0.019	+16.7	+0.007
0.04	0.014	− 8.3	−0.003
0.29	0.087	−15.5	−0.05
0.30	0.066	−12.8	−0.04

10.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.04, 0.19, 0.35, and 0.84 mg P/1, standard deviations were ±0.005, ±0.000, ±0.003, and ±0.000, respectively.

10.3 In a single laboratory (EMSL), using surface water samples at concentrations of 0.07 and 0.76 mg p/1, recoveries were 99% and 100%, respectively.

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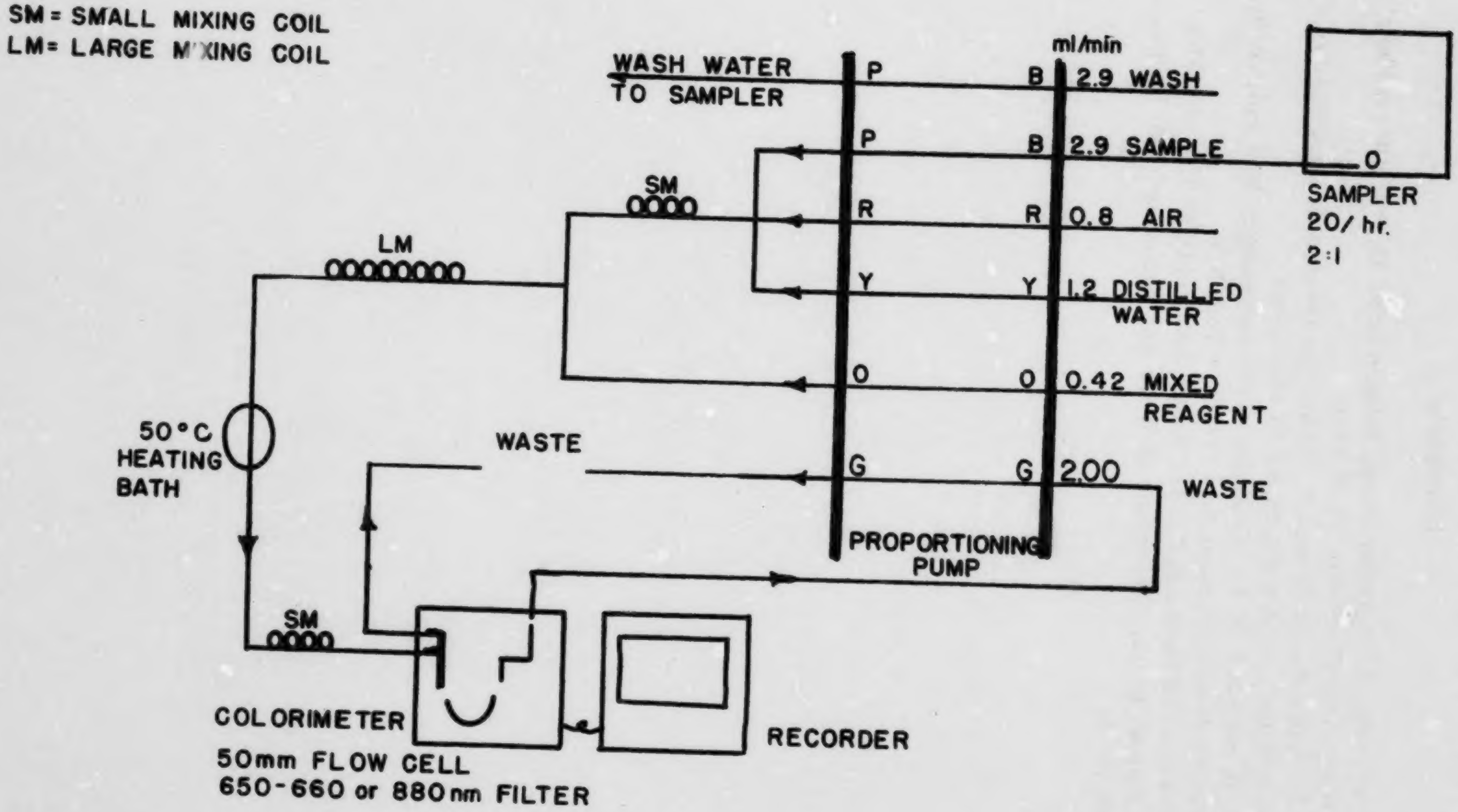
SM = SMALL MIXING COIL
LM = LARGE MIXING COIL
WASH WATER TO SAMPLER
ml/min
P
P
R
Y
O
G
B 2.9 WASH
B 2.9 SAMPLE
R 0.8 AIR
Y 1.2 DISTILLED WATER
O 0.42 MIXED REAGENT
G 2.00
WASTE
SAMPLER
20/ hr.
2:1
O
SM
LM
50°C HEATING BATH
WASTE
PROPORTIONING PUMP
SM
COLORIMETER
50mm FLOW CELL
650-660 or 880nm FILTER
RECORDER

FIGURE 2 PHOSPHORUS MANIFOLD AA I

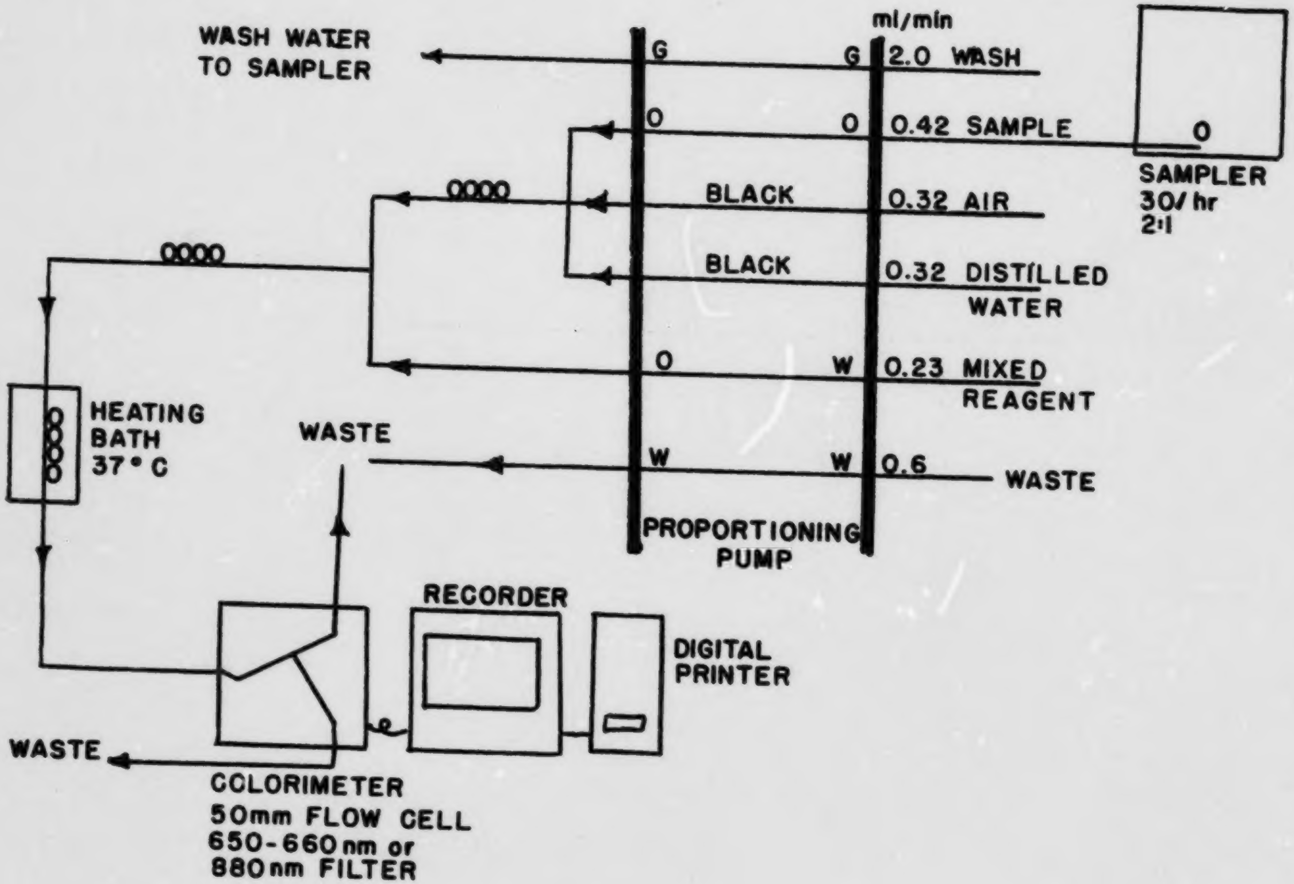
WASH WATER TO SAMPLER
ml/min
G
G
2.0 WASH
O
O
0.42 SAMPLE
SAMPLER 30/hr 2:1
O
BLACK
0.32 AIR
BLACK
0.32 DISTILLED WATER
0000
0000
O
W
0.23 MIXED REAGENT
HEATING BATH 37° C
WASTE
W
W
0.6
WASTE
PROPORTIONING PUMP
RECORDER
DIGITAL PRINTER
WASTE
COLORIMETER 50mm FLOW CELL 650-660 nm or 880 nm FILTER

FIGURE 3 PHOSPHORUS MANIFOLD AA II

PHOSPHORUS, ALL FORMS

Method 365.2 (Colorimetric, Ascorbic Acid, Single Reagent)

STORET NO. See Section 4

1. Scope and Application

1.1 These methods cover the determination of specified forms of phosphorus in drinking, surface and saline waters, domestic and industrial wastes.

1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are defined in Section 4.

1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus are determined by calculation.

1.3 The methods are usable in the 0.01 to 0.5 mg P/1 range.

2. Summary of Method

2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric acid hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion(2).

3. Sample Handling and Preservation

3.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

3.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.

3.3 If the analysis cannot be performed the day of collection, the sample should be preserved by the addition of 2 ml conc. H_2SO_4 per liter and refrigeration at 4°C.

4. Definitions and Storet Numbers

4.1 Total Phosphorus (P) — all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure. (00665)

4.1.1 Total Orthophosphate (P, ortho) — inorganic phosphorus $[(PO_4)^{-3}]$ in the sample as measured by the direct colorimetric analysis procedure. (70507)

4.1.2 Total Hydrolyzable Phosphorus (P, hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphorus. $[(P_2O_7)^{-4}, (P_3O_{10})^{-5}$, etc.] plus some organic phosphorus. (00669)

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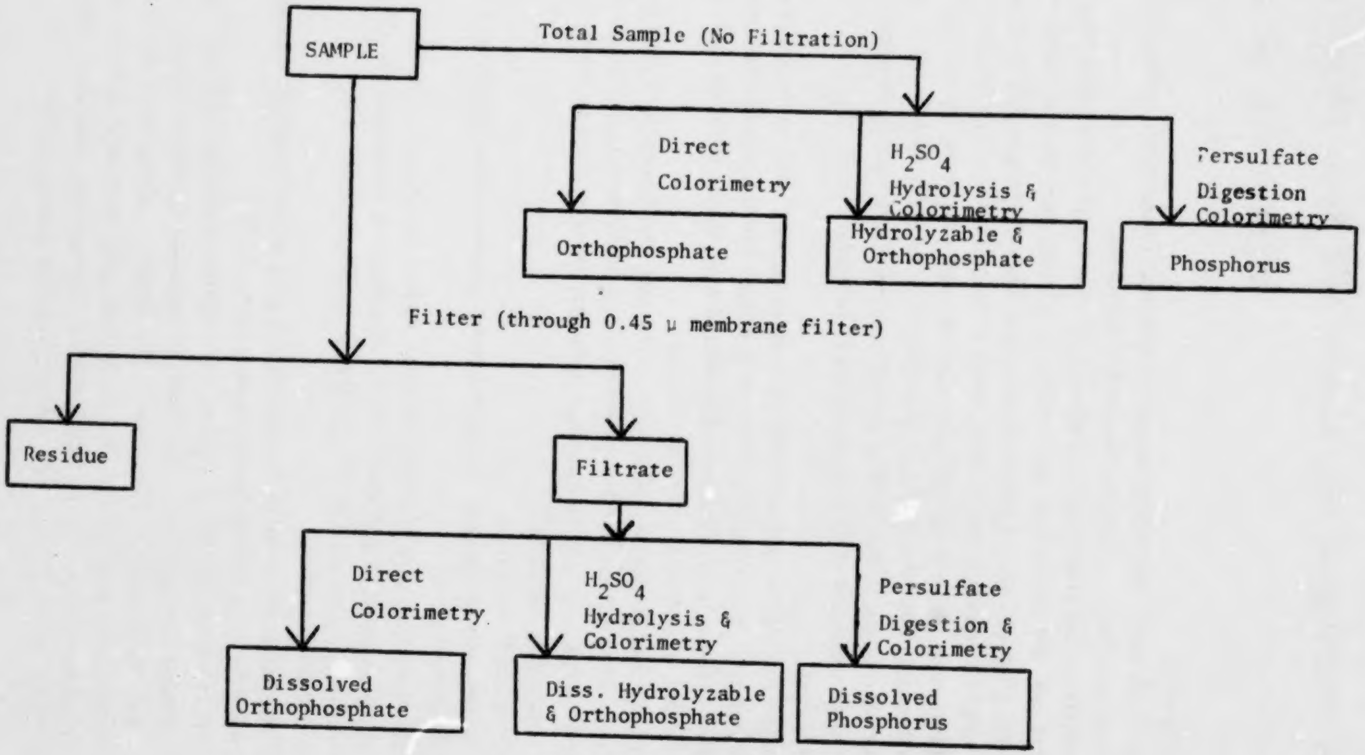
SAMPLE
Total Sample (No Filtration)
Direct
Colorimetry
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Hydrolyzable &
Orthophosphate
Persulfate
Digestion
Colorimetry
Phosphorus
Filter (through 0.45 μ membrane filter)
Residue
Filtrate
Direct
Colorimetry
Dissolved
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Diss. Hydrolyzable
& Orthophosphate
Persulfate
Digestion &
Colorimetry
Dissolved
Phosphorus

FIGURE 1. ANALYTICAL SCHEME FOR DIFFERENTIATION OF PHOSPHORUS FORMS

4.1.3 Total Organic Phosphorus (P, org) — phosphorus (inorganic plus oxidizable organic) in the sample measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)

4.2 Dissolved Phosphorus (P–D) — all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)

4.2.1 Dissolved Orthophosphate (P–D, ortho) — as measured by the direct colorimetric analysis procedure. (00671)

4.2.2 Dissolved Hydrolyzable Phosphorus (P–D, hydro) — as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates. (00672)

4.2.3 Dissolved Organic Phosphorus (P–D, org) — as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)

4.3 The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

4.3.1 Insoluble Phosphorus (P-I) = (P)-(P-D). (00667)

4.3.1.1 Insoluble orthophosphate (P-I, ortho) = (P, ortho)-(P-D, ortho). (00674)

4.3.1.2 Insoluble Hydrolyzable Phosphorus (P-I, hydro) = (P, hydro)-(P-D, hydro). (00675)

4.3.1.3 Insoluble Organic Phosphorus (P-I, org) = (P, org) – (P-D, org). (00676)

4.4 All phosphorus forms shall be reported as P, mg/1, to the third place.

5. Interferences

5.1 No interference is caused by copper, iron, or silicate at concentrations many times greater than their reported concentration in sea water. However, high iron concentrations can cause precipitation of and subsequent loss of phosphorus.

5.2 The salt error for samples ranging from 5 to 20% salt content was found to be less than 1%.

5.3 Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus. However, at concentrations found in sea water, it does not interfere.

6. Apparatus

6.1 Photometer – A spectrophotometer or filter photometer suitable for measurements at 650 or 880 nm with a light path of 1 cm or longer.

6.2 Acid-washed glassware: All glassware used should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

7. Reagents

7.1 Sulfuric acid solution, 5N: Dilute 70 ml of conc. H_2SO_4 with distilled water to 500 ml.

7.2 Antimony potassium tartrate solution: Weigh 1.3715 g $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$, dissolve in 400 ml distilled water in 500 ml volumetric flask, dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 20 g$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 ml of distilled water. Store in a plastic bottle at 4°C.

7.4 Ascorbic acid, 0.1M: Dissolve 1.76 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at 4°C.

7.5 Combined reagent: Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N H_2SO_4, (7.1), 5 ml of antimony potassium tartrate solution (7.2), 15 ml of ammonium molybdate solution (7.3), and 30 ml of ascorbic acid solution (7.4). Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until the turbidity disappears before proceeding. Since the stability of this solution is limited, it must be freshly prepared for each run.

7.6 Sulfuric acid solution, 11 N: Slowly add 310 ml conc. H_2SO_4 to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Stock phosphorus solution: Dissolve in distilled water 0.2197 g of potassium dihydrogen phosphate, KH_2PO_4, which has been dried in an oven at 105°C. Dilute the solution to 1000 ml; 1.0 ml = 0.05 mg P.

7.9 Standard phosphorus solution: Dilute 10.0 ml of stock phosphorus solution (7.8) to 1000 ml with distilled water; 1.0 ml = 0.5 ug P.

7.9.1 Using standard solution, prepare the following standards in 50.0 ml volumetric flasks:

ml of Standard Phosphorus Solution (7.9)	Conc., mg/l
0	0.00
1.0	0.01
3.0	0.03
5.0	0.05
10.0	0.10
20.0	0.20
30.0	0.30
40.0	0.40
50.0	0.50

7.10 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in 600 ml distilled water. Cool and dilute to 1 liter.

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of H_2SO_4 solution (7.6) to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.1.2 Add 0.4 g of ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30–40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15–20 psi).

8.1.4 Cool and dilute the sample to about 30 ml and adjust the pH of the sample to 7.0 ±0.2 with 1 N NaOH (7.10) using a pH meter. If sample is not clear at this point, add 2–3 drops of acid (7.6) and filter. Dilute to 50 ml.
Alternatively, if autoclaved see **NOTE 1**.

8.1.5 Determine phosphorus as outlined in 8.3.2 Orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of H_2SO_4 solution (7.6) to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for 30–40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15–20 psi).

8.2.3 Cool and dilute the sample to about 30 ml and adjust the pH of the sample to 7.0 ±0.2 with NaOH (7.10) using a pH meter. If sample is not clear at this point, add 2–3 drops of acid (7.6) and filter. Dilute to 50 ml.
Alternatively, if autoclaved see **NOTE 1**.

8.2.4 The sample is now ready for determination of phosphorus as outlined in 8.3.2 Orthophosphate.

8.3 Orthophosphate

8.3.1 The pH of the sample must be adjusted to 7±0.2 using a pH meter.

8.3.2 Add 8.0 ml of combined reagent (7.5) to sample and mix thoroughly. After a minimum of ten minutes, but no longer than thirty minutes, measure the color absorbance of each sample at 650 or 880 nm with a spectrophotometer, using the reagent blank as the reference solution.

NOTE 1: If the same volume of sodium hydroxide solution is not used to adjust the pH of the standards and samples, a volume correction has to be employed.

9. Calculation

9.1 Prepare a standard curve by plotting the absorbance values of standards versus the corresponding phosphorus concentrations.

9.1.1 Process standards and blank exactly as the samples. Run at least a blank and two standards with each series of samples. If the standards do not agree within ±2% of the true value, prepare a new calibration curve.

9.2 Obtain concentration value of sample directly from prepared standard curve. Report results as P, mg/1. **SEE NOTE 1.**

10. Precision and Accuracy

10.1 Thirty-three analysts in nineteen laboratories analyzed natural water samples containing exact increments of organic phosphate, with the following results:

Increment as Total Phosphorus mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as	
		Bias, %	Bias mg P/liter
0.110	0.033	+3.09	+0.003
0.132	0.051	+11.99	+0.016
0.772	0.130	+2.96	+0.023
0.882	0.128	–0.92	–0.008

(FWPCA Method Study 2, Nutrient Analyses)

10.2 Twenty-six analysts in sixteen laboratories analyzed natural water samples containing exact increments of orthophosphate, with the following results:

Increment as Orthophosphate mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as	
		Bias, %	Bias, mg P/liter
0.029	0.010	–4.95	–0.001
0.038	0.008	–6.00	–0.002
0.335	0.018	–2.75	–0.009
0.383	0.023	–1.76	–0.007

(FWPCA Method Study 2, Nutrient Analyses)

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PHOSPHORUS, ALL FORMS

Method 365.3 (Colorimetric, Ascorbic Acid, Two Reagent)

STORET NO. See Section 4

1. Scope and Application
   1.1 These methods cover the determination of specified forms of phosphorus in drinking, surface and saline waters, domestic and industrial wastes.
   1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pretreatment of the sample, the various forms may be determined.
      1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus are determined by calculation.
   1.3 The methods are usable in the 0.01 to 1.2 mg P/1 range.
2. Summary of Method
   2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.
   2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric-acid-hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion.
3. Sample Handling and Preservation
   3.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.
   3.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.
   3.3 If the analysis cannot be performed the day of collection, the sample should be preserved by the addition of 2 ml conc. H_2SO_4 per liter and refrigeration at 4°C.
4. Definitions and Storet Numbers
   4.1 Total Phosphorus (P) — all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure. (00665)
      4.1.1 Total Orthophosphate (P, ortho) — inorganic phosphorus $[(PO_4)^{-3}]$ in the sample as measured by the direct colorimetric analysis procedure. (70507)
      4.1.2 Total Hydrolyzable Phosphorus (P, hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphorus. $[(P_2O_7)^{-4}, (P_3O_{10})^{-5}$, etc.] plus some organic phosphorus. (00669)

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4.1.3 Total Organic Phosphorus (P, org) — phosphorus (inorganic plus oxidizable organic) in the sample measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)

4.2 Dissolved Phosphorus (P–D) — all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)

4.2.1 Dissolved Orthophosphate (P–D, ortho) — as measured by the direct colorimetric analysis procedure. (00671)

4.2.2 Dissolved Hydrolyzable Phosphorus (P–D, hydro) — as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates. (00672)

4.2.3 Dissolved Organic Phosphorus (P–D, org) — as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)

4.3 The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

4.3.1 Insoluble Phosphorus (P-I)=(P)-(P-D). (00667)

4.3.1.1 Insoluble orthophosphate (P-I, ortho)=(P, ortho) - (P-D, ortho). (00674)

4.3.1.2 Insoluble Hydrolyzable Phosphorus (P–I, hydro)=(P, hydro) - (P–D, hydro). (00675)

4.3.1.3 Insoluble Organic Phosphorus (P–I, org)=(P, org) - (P-D, org). (00676)

4.4 All phosphorus forms shall be reported as P, mg/1, to the third place.

5. Interferences

5.1 Arsenate is determined similarily to phosphorus and should be considered when present. This interference may be eliminated by reducing the arsenic acid to arsenious acid with sodium bisulfite (7.4).

5.2 When high concentrations of iron are present low recovery of phosphorus will be obtained because it will use some of the reducing agent. The bisulfite treatment will also eliminate this interference.

6. Apparatus

6.1 Photometer–A spectrophotometer or filter photometer suitable for measurements at 660 or 880 nm with a light path of 1 cm or longer.

6.2 Acid-washed glassware: All glassware used should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be absorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

6.3 Water bath, 95°C.

7. Reagents

7.1 Ammonium molybdate-antimony potassium tartrate solution: Dissolve 8 g of ammonium molybdate and 0.2 g antimony potassium tartrate in 800 ml of distilled water and dilute to 1 liter.

7.2 Ascorbic acid solution: Dissolve 60 g of ascorbic acid in 800 ml of distilled water and dilute to 1 liter. Add 2 ml of acetone. This solution is stable for two weeks.

7.3 Sulfuric acid, 11 N: Slowly add 310 ml of conc. H_2SO_4 to approximately 600 ml distilled water. Cool and dilute to 1000 ml.

7.4 Sodium bisulfite ($NaHSO_3$) solution: Dissolve 5.2 g of $NaHSO_3$ in 100 ml of 1.0 N H_2SO_4.

7.5 Ammonium persulfate.

7.6 Stock phosphorus solution: Dissolve 0.4393 g of predried (105°C for one hour) KH_2PO_4 in distilled water and dilute to 1000 ml. 1.0 ml = 0.1 mg P.

7.7 Standard phosphorus solution: Dilute 100 ml of stock phosphorus solution to 1000 ml with distilled water. 1.0 ml = 0.01 mg P. Prepare an appropriate series of standards by diluting suitable volumes of standard or stock solutions to 100 ml with distilled water.

8. Procedure

8.1 Total Phosphorus

8.1.1 Transfer 50 ml of sample or an aliquot diluted to 50 ml into a 125 ml Erlenmeyer flask and add 1 ml of 11 N sulfuric acid (7.3).

8.1.2 Add 0.4 g ammonium persulfate (7.5), mix and boil gently for approximately 30–40 minutes or until a final volume of about 10 ml is reached. Alternatively heat for 30 minutes in an autoclave at 121°C (15–20 psi). Cool, dilute to approximately 40 ml and filter.

8.1.3 For samples containing arsenic or high levels of iron, add 5 ml of sodium bisulfite (7.4), mix and place in a 95°C water bath for 30 minutes (20 minutes after the temperature of the sample reaches 95°C). Cool and dilute to 50 ml.

8.1.4 Determine phosphorus as outlined in (8.3) orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of H_2SO_4 solution (8.3) to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for 30–40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15–20 psi). Cool, dilute to approximately 40 ml and filter.

8.2.3 Treat the samples as in 8.1.3.

8.2.4 Determine phosphorus as outlined in (8.3) orthophosphate.

8.3 Orthophosphate

8.3.1 To 50 ml of sample and/or standards, add 1 ml of 11 N sulfuric acid (7.3) and 4 ml of ammonium molybdate-antimony potassium tartrate (7.1) and mix.
NOTE: If sample has been digested for total or hydrolyzable phosphorus do not add acid.

8.3.2 Add 2 ml of ascorbic acid solution (7.2) and mix.

8.3.3 After 5 minutes, measure the absorbance at 650 nm with a spectrophotometer and determine the phosphorus concentration from the standard curve. The color is stable for at least one hour. For concentrations in the range of 0.01 to 0.3 mg P/1, a 5 cm cell should be used. A one cm cell should be used for concentrations in the range of 0.3 to 1.2 mg P/1.

9. Calculation

9.1 Prepare a standard curve by plotting the absorbance values of standards versus the corresponding phosphorus concentrations on linear graph paper.

9.2 Obtain concentration value of sample directly from prepared standard curve. Report results as P, mg/1.

10. Precision and Accuracy

10.1 Precision data is not available at this time.

10.2 In a single laboratory (EMSL) using industrial waste and sewage samples at concentrations of 7.6 and 0.55 mg P/1, recoveries were 99 and 100%, respectively.

PHOSPHORUS, TOTAL

Method 365.4 (Colorimetric, Automated, Block Digestor AA II)

STORET NO. 00665

1. Scope and Application

   1.1 This method covers the determination of total phosphorus in drinking water, surface water and domestic and industrial wastes. The applicable range of this method is 0.01 to 20 mg P/1.

2. Summary of Method

   2.1 The sample is heated in the presence of sulfuric acid, K_2SO_4 and $HgSO_4$ for two and one half hours. The residue is cooled, diluted to 25 ml and placed on the AutoAnalyzer for phosphorus determination.

3. Sample Handling and Preservation

   3.1 Sample containers may be of plastic material, such as a cubitainer, or of Pyrex glass.

   3.2 If the analysis cannot be performed the day of collection, the sample should be preserved by the addition of 2 ml of conc. H_2SO_4 per liter and refrigeration at 4°C.

4. Apparatus

   4.1 Block Digestor BD–40

   4.2 Technicon Method No. 327–74W for Phosphorus

5. Reagents

   5.1 Mercuric sulfate: Dissolve 8 g red mercuric oxide (HgO) in 50 ml of 1:4 sulfuric acid (10 conc. H_2SO_4: 40 ml distilled water) and dilute to 100 ml with distilled water.

   5.2 Digestion solution: (Sulfuric acid-mercuric sulfate-potassium sulfate solution): Dissolve 133 g of K_2SO_4 in 600 ml of distilled water and 200 ml of conc. H_2SO_4. Add 25 ml of mercuric sulfate solution (5.1) and dilute to 1 liter.

   5.3 Sulfuric acid solution (0.72 N): Add 20 ml of conc. sulfuric acid to 800 of distilled water, mix and dilute to 1 liter.

   5.4 Molybdate/antimony solution: Dissolve 8 g of ammonium molybdate and 0.2 g of antimony potassium tartrate in about 800 ml of distilled water and dilute to 1 liter.

   5.5 Ascorbic acid solution: Dissolve 60 g of ascorbic acid in about 600 ml of distilled water. Add 2 ml of acetone and dilute to 1 liter.

   5.6 Diluent water: Dissolve 40 g of NaCl in about 600 ml of distilled water and dilute to 1 liter.

   5.7 Sulfuric acid solution, 4%: Add 40 ml of conc. sulfuric acid to 800 ml of ammonia-free distilled water, cool and dilute to 1 liter.

6. Procedure

   Digestion

   6.1 To 20 or 25 ml of sample, add 5 ml of digestion solution and mix. (Use a vortex mixer).

   6.2 Add 4–8 Teflon boiling chips. Too many boiling chips will cause the sample to boil over.

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6.3 With Block Digestor in manual mode set low and high temperature at 160°C and preheat unit to 160°C. Place tubes in digestor and switch to automatic mode. Set low temperature timer for 1 hour. Reset high temperature to 380°C and set timer for 2 1/2 hours.

6.4 Cool sample and dilute to 25 ml with distilled water. If TKN is determined the sample should be diluted with ammonia-free water.

Colorimetric Analysis

6.4.1 Check the level of all reagent containers to ensure an adequate supply.

6.4.2 Excluding the molybdate/antimony line, place all reagent lines in their respective containers, connect the sample probe to the Sampler IV and start the proportioning pump.

6.4.3 Flush the Sampler IV wash receptacle with about 25 ml of 4% sulfuric acid (5.7).

6.4.4 When reagents have been pumping for at least five minutes, place the molybdate/antimony line in its container and allow the system to equilibrate.

6.4.5 After a stable baseline has been obtained, start the sampler.

7. Calculations

7.1 Prepare a standard curve by plotting peak heights of processed standards against concentration values. Compute concentrations by comparing sample peak heights with the standard curve.

8. Precision and Accuracy

8.1 In a single laboratory (EMSL) using sewage sample containing total P at levels of 0.23, 1.33, and 2.0, the precision was ±0.01, ±0.04, and ±0.06, respectively.

8.2 In a single laboratory (EMSL) using sewage samples of concentration 1.84 and 1.89, the recoveries were 95 and 98%, respectively.

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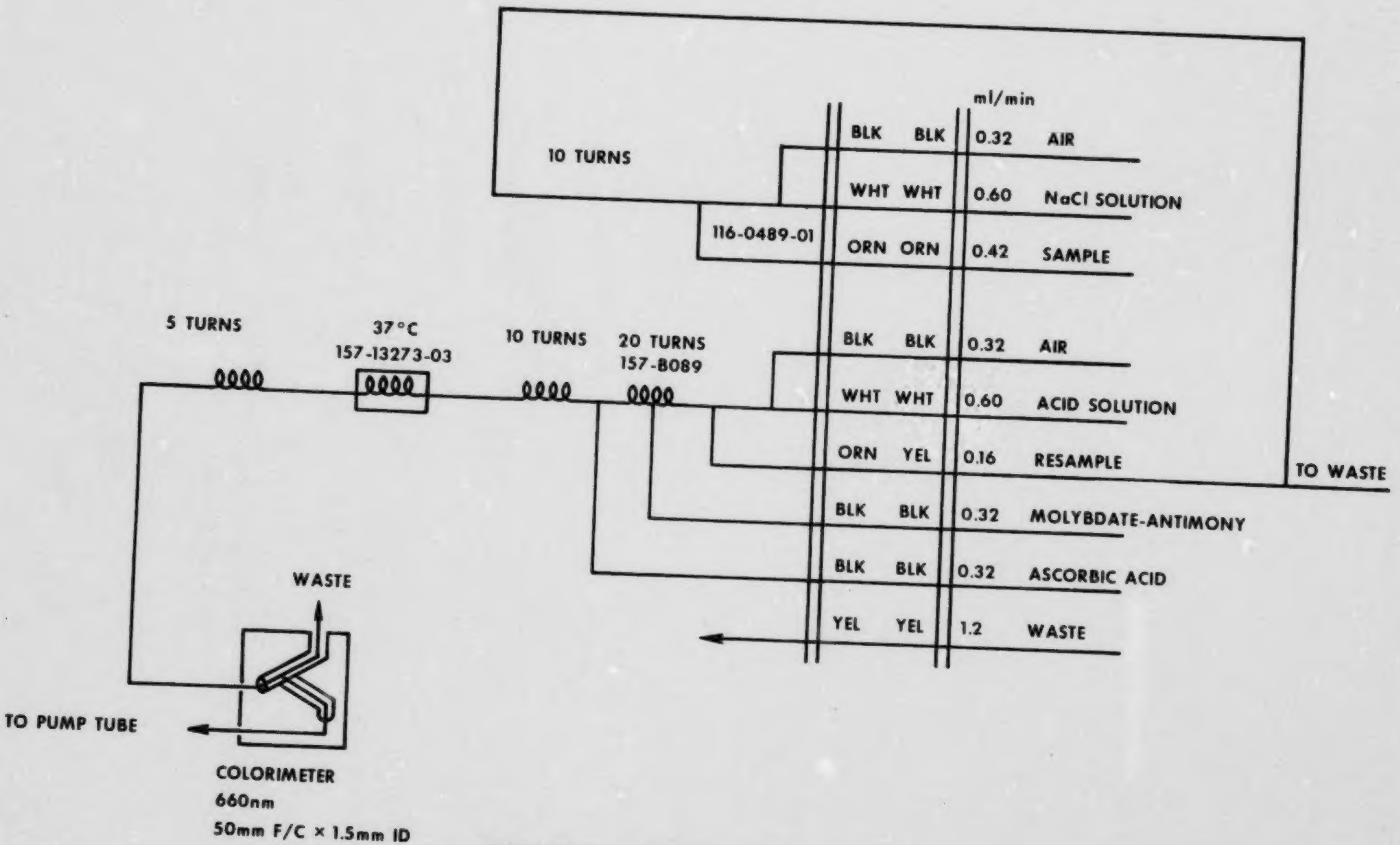
ml/min
BLK BLK 0.32 AIR
WHT WHT 0.60 NaCl SOLUTION
ORN ORN 0.42 SAMPLE
BLK BLK 0.32 AIR
WHT WHT 0.60 ACID SOLUTION
ORN YEL 0.16 RESAMPLE
BLK BLK 0.32 MOLYBDATE-ANTIMONY
BLK BLK 0.32 ASCORBIC ACID
YEL YEL 1.2 WASTE
TO WASTE
10 TURNS
116-0489-01
5 TURNS
37°C
157-13273-03
10 TURNS
20 TURNS
157-B089
WASTE
TO PUMP TUBE
COLORIMETER
660nm
50mm F/C × 1.5mm ID

FIGURE 1. PHOSPHORUS MANIFOLD AA11

SILICA, DISSOLVED

Method 370.1 (Colorimetric)

STORET NO. Dissolved 00955

1. Scope and Application

    1.1 This method is applicable to drinking, surface and saline waters, domestic and industrial wastes.

    1.2 The working range of the method is approximately 2 to 25 mg silica/l. The upper range can be extended by taking suitable aliquots; the lower range can be extended by the addition of amino-naphthol-sulfonic acid solution, as described in (6.8).

2. Summary of Method

    2.1 A well-mixed sample is filtered through a 0.45 *u* membrane filter. The filtrate, upon the addition of molybdate ion in acidic solution, forms a greenish-yellow color complex proportional to the dissolved silica in the sample. The color complex is then measured spectrophotometrically.

    2.2 In the low concentration modification the yellow (410 nm) molybdosilicic acid color is reduced by 1-amino-2-naphthol-4-sulfonic acid to a more intense heteropoly blue (815 nm or 650 nm).

3. Interferences

    3.1 Excessive color and/or turbidity interfere. Correct by running blanks prepared without addition of the ammonium molybdate solution. See (6.7).

    3.2 Tannin interference may be eliminated and phosphate interferences may be decreased with oxalic acid.

    3.3 Large amounts of iron and sulfide interfere.

    3.4 Contact with glass should be minimized, silica free reagents should be used as much as possible. A blank should be run.

4. Apparatus

    4.1 Platinum dishes, 100 ml.

    4.2 Colorimetric equipment–one of the following:

        4.2.1 Spectrophotometer for use at 410 nm, 650 nm and/or 815 nm with a 1 cm or longer cell.

        4.2.2 Filter photometer with a violet filter having maximum transmittance as near 410 nm as possible and a 1 cm or longer cell.

        4.2.3 Nessler tubes, matched, 50 ml, tall form.

5. Reagents

    5.1 Use chemicals low in silica and store in plastic containers.

    5.2 Sodium bicarbonate, $NaHCO_3$, powder.

    5.3 Sulfuric acid, H_2SO_4, 1 N.

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5.4 Hydrochloric acid, HCl, 1 + 1.

5.5 Ammonium molybdate reagent: Place 10 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in distilled water in a 100 ml volumetric. Dissolve by stirring and gently warming. Dilute to the mark. Filter if necessary. Adjust to pH 7 to 8 with silica free NH_4OH or NaOH. Store in plastic bottle.

5.6 Oxalic acid solution: Dissolve 10 g $H_2C_2O_4 \cdot 2H_2O$ in distilled water in a 100 ml volumetric flask, dilute to the mark. Store in plastic.

5.7 Stock silica solution: Dissolve 4.73 g sodium metasilicate nonahydrate, $Na_2SiO_3 \cdot 9H_2O$, in recently boiled and cooled distilled water. Dilute to approximately 900 ml. Analyze 100.0 ml portions by gravimetry (ref. 1, p. 484). Adjust concentration to 1.000 mg/1 SiO_2. Store in tightly stoppered plastic bottle.

5.8 Standard silica solution: Dilute 10.0 ml stock solution to 1 liter with recently boiled and cooled distilled water. This is 10 mg/1 SiO_2 (1.00 ml = 10.0 *ug* SiO_2). Store in a tightly stoppered plastic bottle.

5.9 Permanent color solutions

5.9.1 Potassium chromate solution: Dissolve 630 mg K_2CrO_4 in distilled water in a 1 liter volumetric flask and dilute to the mark.

5.9.2 Borax solution: Dissolve 10 g sodium borate decahydrate, ($Na_2B_4O_7 \cdot 10H_2O$) in distilled water in a 1 liter volumetric flask and dilute to the mark.

5.10 Reducing agent: Dissolve 500 mg of 1-amino-2-naphthol-4-sulfonic acid and 1 g Na_2SO_3 in 50 ml distilled water with gentle warming if necessary. Dissolve 30 g $NaHSO_3$ in 150 ml distilled water. Mix these two solutions. Filter into a plastic bottle. Refrigerate and avoid exposure to light. Discard when it darkens. If there is incomplete solubility or immediate darkening of the aminonaphthosulfonic acid solution do not use.

6. Procedure

6.1 Filter sample through a 0.45 u membrane filter.

6.2 Digestion: If molybdate unreactive silica is present and its inclusion in the analysis is desired, include this step, otherwise proceed to 6.3.

6.2.1 Place 50 ml, or a smaller portion diluted to 50 ml, of filtered (6.1) sample in a 100 ml platinum dish.

6.2.2 Add 200 mg silica-free $NaHCO_3$ (5.2) and digest on a steam bath for 1 hour. Cool.

6.2.3 Add slowly and with stirring 2.4 ml H_2SO_4 (5.3).

6.2.4 Immediately transfer to a 50 ml Nessler tube, dilute to the mark with distilled water and proceed to 6.3 without delay.

6.3 Color development

6.3.1 Place 50 ml sample in a Nessler tube.

6.3.2 Add rapidly 1.0 ml of 1+1 HCl (5.4) and 2.0 ml ammonium molybdate reagent (5.5).

6.3.3 Mix by inverting at least 6 times.

6.3.4 Let stand 5 to 10 minutes.

6.3.5 Add 1.5 ml oxalic acid solution (5.6) and mix thoroughly.

6.3.6 Read color (spectrophotometrically or visually) after 2 minutes but before 15 minutes from the addition of oxalic acid.

6.4 Preparation of Standards

6.4.1 If digestion (6.2) was used add 200 mg $NaHCO_3$ (5.2) and 2.4 ml H_2SO_4 (5.3) to standards to compensate for silica introduced by these reagents and for effect of the salt on the color intensity.

6.5 Photometric measurement

6.5.1 Prepare a calibration curve using approximately six standards to span the range shown below with the selected light path.

Selection of Light Path Length for Various Silica Concentrations

Light Path cm	Silica in 54.5 ml final volume (*ug*)
1	200–1300
2	100–700
5	40–250
10	20–130

6.5.2 Carry out the steps in 6.3 using distilled water as the reference. Read a blank.

6.5.3 Plot photometric reading versus *ug* of silica in the final solution of 54.5 ml. Run a reagent blank and at least one standard with each group of samples.

6.6 Visual Comparison

6.6.1 Prepare a set of permanent artificial color standards according to the table. Use well stoppered, properly labelled 50 ml Nessler tubes.

Silica value mg	Potassium chromate solution (5.9.1) ml	Borax solution (5.9.2) ml	Distilled water ml
0.00	0.0	25	30
0.10	1.0	25	29
0.20	2.0	25	28
0.40	4.0	25	26
0.50	5.0	25	25
0.75	7.5	25	22
1.00	10.0	25	20

6.6.2 Verify permanent standards by comparison to color developed by standard silica solutions.

6.6.3 These permanent artificial color standards are only for color comparison procedure, not for photometric procedure.

6.7 Correction for color or turbidity

6.7.1 A special blank is run using a portion of the sample and carrying out the procedure in 6.1, 6.2 if used, and 6.3 except for the addition of ammonium molybdate (6.3.2).

6.7.2 Zero the photometer with this blank before reading the samples.

6.8 Procedure for low concentration (< 1000 *ug*/l)

6.8.1 Perform steps 6.1 and 6.2 if needed.

6.8.2 Place 50 ml sample in a Nessler tube.

6.8.3 In rapid succession add 1.0 ml of 1 + 1 HCl (5.4).

6.8.4 Add 2.0 ml ammonium molybdate reagent (5.5).

6.8.5 Mix by inverting at least six times.

6.8.6 Let stand 5 to 10 minutes.

6.8.7 Add 1.5 ml oxalic acid solution (5.6).

6.8.8 Mix thoroughly.

6.8.9 At least 2, but not more than 15 minutes after oxalic acid addition, add 2.0 ml reducing agent (5.10).

6.8.10 Mix thoroughly.

6.8.11 Wait 5 minutes, read photometrically or visually.

6.8.12 If digestion (6.2) was used see (6.4).

6.8.13 Photometric measurement

6.8.13.1 Prepare a calibration curve using approximately 6 standards and a reagent blank to span the range shown below with the selected light path.

Selection of Light Path Length for
Various Silica Concentrations

Light Path cm	Silica in 56.5 ml Final volume, *ug*	
	650 nm	815 nm
1	40–300	20–100
2	20–150	10–50
5	7–50	4–20
10	4–30	2–10

6.8.13.2 Read versus distilled water.

6.8.13.3 Plot photometric reading at 650 nm or at 815 nm versus *ug* of silica in 56.5 ml.

6.8.13.4 For turbidity correction use 6.1, 6.2 if used and 6.8.2–6.8.11 omitting 6.8.4 and 6.8.9.

6.8.13.5 Run a reagent blank and at least one standard (to check calibration curve drift) with each group of samples.

6.8.14 Visual comparison

6.8.14.1 Prepare not less than 12 standards covering the range of 0 to 120 *ug* SiO_2 by placing the calculated volumes of standard silica (5.8) in 50 ml Nessler tubes, diluting to the mark and develop the color as in 6.8.2–6.8.11.

7. Calculations

7.1 Read ug SiO_2 from calibration curve or by visual comparison

7.2 mg/l SiO_2 =

$$\frac{\text{ug SiO}_2}{\text{ml sample}}$$

7.3 Report whether $NaHCO_3$ digestion (6.2) was used

8. Precision and Accuracy

8.1 A synthetic unknown sample containing 5.0 mg/l SiO_2, 10 mg/l chloride, 0.200 mg/l ammonia N, 1.0 mg/l nitrate N, 1.5 mg/l organic N, and 10.0 mg/l phosphate in distilled water was analyzed in 19 laboratories by the molybdosilicate method, with a relative standard deviation of 14.3% and a relative error of 7.8%.

8.2 Another synthetic unknown sample containing 15.0 mg/l SiO_2, 200 mg/l chloride, 0.800 mg/l ammonia N, 1.0 mg/l nitrate N, 0.800 mg/l organic N, and 5.0 mg/l phosphate in distilled water was analyzed in 19 laboratories by the molybdosilicate method, with a relative standard deviation of 8.4% and a relative error of 4.2%.

8.3 A third synthetic unknown sample containing 30.0 mg/l SiO_2, 400 mg/l chloride, 1.50 mg/l ammonia N, 1.0 mg/l nitrate N, 0.200 mg/l organic N, and 0.500 mg/l phosphate in distilled water was analyzed in 20 laboratories by the molybdosilicate method, with a relative standard deviation of 7.7% and a relative error of 9.8%. All results were obtained after sample digestion with $NaHCO_3$.

8.4 Photometric evaluations by the amino-naphthol-sulfonic acid procedure have an estimated precision of ±0.10 mg/l in the range from 0 to 2 mg/l (ASTM).

8.5 Photometric evaluations of the silico-molybdate color in the range from 2 to 50 mg/l have an estimated precision of approximately 4% of the quantity of silica measured (ASTM).

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1. Annual Book of ASTM Standards, Part 31, "Water", Standard D859–68, p 401 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 487, Method 426B, (1975).

SULFATE

Method 375.1 (Colorimetric, Automated, Chloranilate)

STORET NO. Total 00945

1. Scope and Application
   1.1 This automated method is applicable to drinking and surface waters, domestic and industrial wastes, in the range of 10 to 400 mg SO_4/1. Approximately 15 samples per hour can be analyzed.
2. Summary of Method
   2.1 When solid barium chloranilate is added to a solution containing sulfate, barium sulfate is precipitated, releasing the highly colored acid chloranilate ion. The color intensity in the resulting chloranilic acid is proportional to the amount of sulfate present.
3. Sample Handling and Preservation
   3.1 Refrigeration at 4°C.
4. Interferences
   4.1 Cations, such as calcium, aluminum, and iron, interfere by precipitating the chloranilate. These ions are removed automatically by passage through an ion exchange column.
5. Apparatus
   5.1 Technicon AutoAnalyzer consisting of:
      5.1.1 Sampler I.
      5.1.2 Continuous filter.
      5.1.3 Manifold.
      5.1.4 Proportioning pump.
      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters.
      5.1.6 Recorder.
      5.1.7 Heating bath, 45°C.
   5.2 Magnetic stirrer.
6. Reagents
   6.1 Barium chloranilate: Add 9 g of barium chloranilate ($BaC_6Cl_2O_4$) to 333 ml of ethyl alcohol and dilute to 1 liter with distilled water.
   6.2 Acetate buffer, pH 4.63: Dissolve 13.6 g of sodium acetate in distilled water. Add 6.4 ml of acetic acid and dilute to 1 liter with distilled water. Make fresh weekly.
   6.3 NaOH-EDTA solution: Dissolve 65 g of NaOH and 6 g of EDTA in distilled water and dilute to 1 liter.
   NOTE 1: This solution is also used to clean out manifold system at end of sampling run.
   6.4 Ion exchange resin: Dowex-50 W-X8, ionic form-H^+.
   NOTE 2: Column is prepared by sucking a slurry of the resin into 12 inches of 3/16-inch OD sleeving. This may be conveniently done by using a pipette and a loose-fitting glass wool plug in the sleeve. The column, upon exhaustion, turns red.

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6.5 Stock solution: Dissolve 1.4790 g of oven-dried (105°C) Na_2SO_4 in distilled water and dilute to 1 liter in a volumetric flask. 1.0 ml = 1.0 mg.

6.5.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/l
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
15.0	150
20.0	200
30.0	300
40.0	400

7. Procedure

7.1 Set up manifold as shown in Figure 1. (Note that any precipitated $BaSO_4$ and the unused barium chloranilate are removed by filtration. If any $BaSO_4$ should come through the filter, it is complexed by the NaOH–EDTA reagent).

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.

7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 39, 111, 188 and 294 mg SO_4/1, the standard deviations were ±0.6, ±1.0, ±2.2 and ±0.8, respectively.

9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 82 and 295 mg SO_4/1, recoveries were 99% and 102%, respectively.

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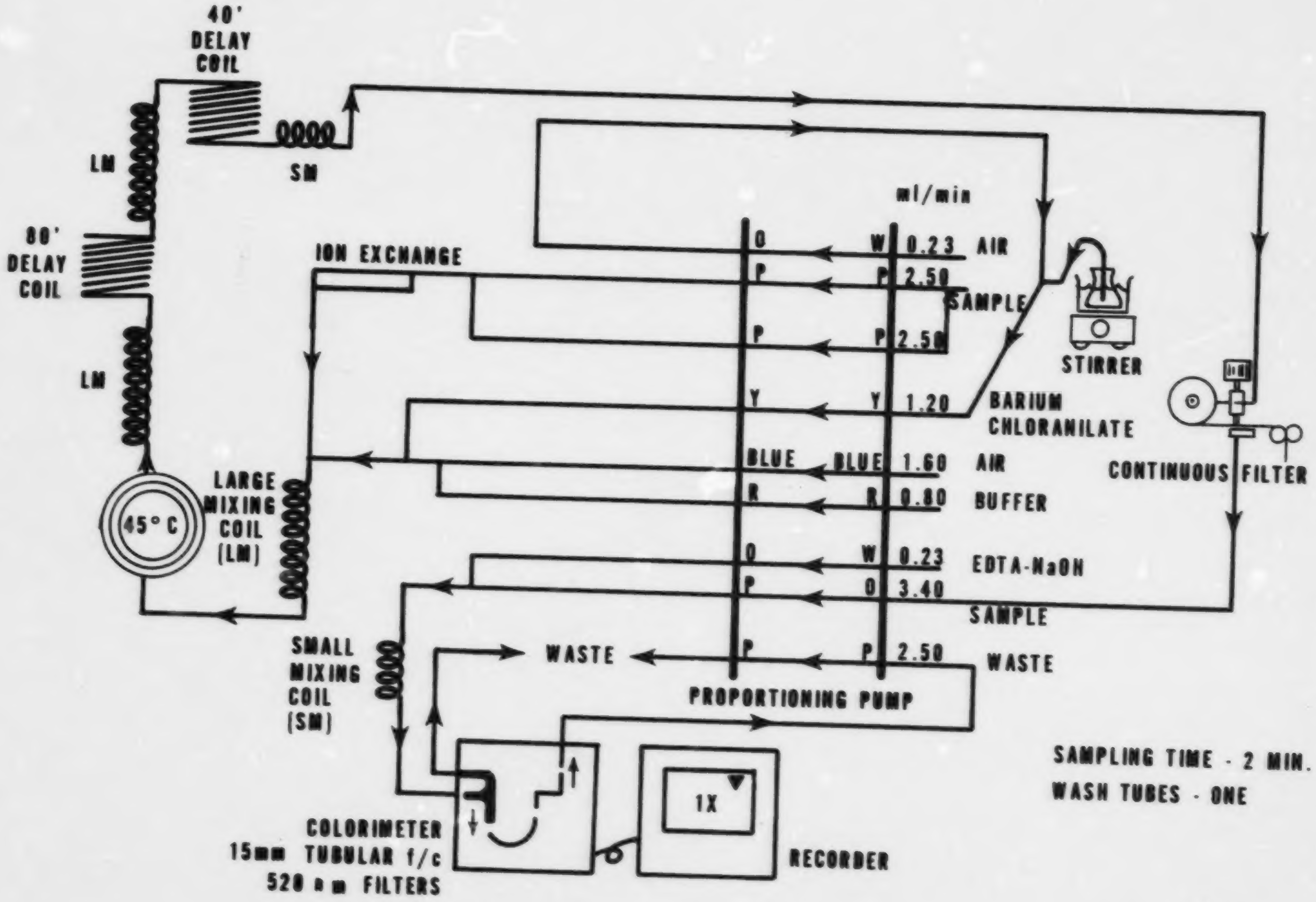
40' DELAY COIL
SM
LM
80' DELAY COIL
LM
45° C
LARGE MIXING COIL (LM)
ION EXCHANGE
ml/min
O
W 0.23 AIR
P
P 2.50
SAMPLE
P
P 2.50
Y
Y 1.20 BARIUM CHLORANILATE
STIRRER
BLUE
BLUE 1.60 AIR
R
R 0.80 BUFFER
CONTINUOUS FILTER
O
W 0.23 EDTA-NaOH
P
O 3.40 SAMPLE
P
P 2.50 WASTE
WASTE
PROPORTIONING PUMP
SMALL MIXING COIL (SM)
COLORIMETER 15mm TUBULAR f/c 520 nm FILTERS
1X
RECORDER

SAMPLING TIME - 2 MIN.
WASH TUBES - ONE

FIGURE 1 - SULFATE MANIFOLD AA-I

SULFATE

Method 375.2 (Colorimetric, Automated, Methylthymol Blue, AA II)

STORET NO. 00945

1. Scope and Application
   - 1.1 This automated method is applicable to drinking and surface waters, domestic and industrial wastes.
   - 1.2 Samples in the range of 3 to 300 mg $SO_4/1$ can be analyzed. The sensitivity of the method can be increased by a minor modification to analyze samples in the range of 0.5 to 30 mg $SO_4/1$. Approximately 30 samples per hour can be analyzed.
2. Summary of Method
   - 2.1 The sample is first passed through a sodium form cation-exchange column to remove multivalent metal ions. The sample containing sulfate is then reacted with an alcohol solution of barium chloride and methylthymol blue (MTB) at a pH of 2.5–3.0 to form barium sulfate. The combined solution is raised to a pH of 12.5–13.0 so that excess barium reacts with MTB. The uncomplexed MTB color is gray; if it is all chelated with barium, the color is blue. Initially, the barium and MTB are equimolar and equivalent to 300 mg $SO_4/1$; thus the amount of uncomplexed MTB is equal to the sulfate present.
3. Sample Handling and Preservation
   - 3.1 Refrigeration at 4°C.
4. Interferences
   - 4.1 The ion exchange column eliminates interferences from multivalent cations. A mid-scale sulfate standard containing Ca^{++} should be analyzed periodically to insure that the column is functioning properly.
   - 4.2 Samples with pH below 2 should be neutralized because high acid concentrations elute cations from the ion exchange resin.
   - 4.3 Turbid samples should be filtered or centrifuged.
5. Apparatus
   - 5.1 Technicon Auto Analyzer consisting of:
     - 5.1.1 Sampler
     - 5.1.2 Manifold–high or low level (Figure I)
     - 5.1.3 Proportioning pump
     - 5.1.4 Colorimeter equipped with 15 mm flow cell and 460 nm interference filters.
     - 5.1.5 Recorder
     - 5.1.6 Digital Printer for AAII (optional)
6. Reagents
   - 6.1 Barium chloride: Dissolve 1.526 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 500 ml of distilled water and dilute to 1 liter.

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6.2 Methylthymol blue: Dissolve 0.1182 g of methylthymol blue (3'3”-bis-N,N-bis carboxymethyl)–amino methylthymolsulfone-phthalein pentasodium salt) in 25 ml of barium chloride solution (6.1). Add 4 ml of 1.0 N hydrochloric acid which changes the color to bright orange. Add 71 ml of water and dilute to 500 ml with ethanol. The pH of this solution is 2.6. This reagent should be prepared the day before and stored in a brown plastic bottle in the refrigerator.

6.3 Buffer, pH 10.5 ± 0.5: Dissolve 6.75 g of ammonium chloride in 500 ml of distilled water. Add 57 ml of concentrated ammonium hydroxide and dilute to one liter with distilled water.

6.4 Buffered EDTA: Dissolve 40 g of tetrasodium EDTA in pH 10.5 buffer (6.3), and dilute to one liter with buffer.

6.5 Sodium hydroxide solution, (50%): Dissolve 500 g NaOH in 600 ml of distilled water, cool, and dilute to 1 liter.

6.6 Sodium hydroxide, 0.18N: Dilute 14.4 ml of sodium hydroxide solution (6.5) to 1 liter.

6.7 Ion exchange resin: Bio-Rex 70, 20–50 mesh, sodium form, Bio-Rad Laboratories, Richmond, California. Free from fines by stirring with several portions of deionized water and decant the supernate before settling is complete.

6.8 Dilution Water: Add 0.75 ml of sulfate stock solution (6.9) and 3 drops of Brij-35 to 2 liters of distilled water.

6.9 Sulfate stock solution, 1 ml = 1 mg SO_4: Dissolve 1.479 g of dried (105°C) Na_2SO_4 in distilled water and dilute to 1 liter.

6.10 Dilute sulfate solution, 1 ml = 0.1 mg SO_4: Dilute 100 ml of sulfate stock solution (6.9) to 1 liter.

6.11 High level working standards, 10–300 mg/1: Prepare high level working standards by diluting the following volumes of stock standard (6.9) to 100 ml.

ml stock	mg/l SO_4
1	10
5	50
10	100
15	150
25	250
30	300

6.12 Low level working standards, 1–30 mg/1: Prepare low level working standards by diluting the following volumes of dilute sulfate solution (6.10) to 100 ml.

ml stock	mg/l SO_4
1	1.0
5	5.0
10	10.0
15	15.0
25	25.0
30	30.0

7. Procedure

7.1 Set up the manifold for high (0–300 mg SO_4/l) or low (0–30 mg SO_4/l) level samples as described in Figure I.

7.2 The ion exchange column is prepared by pulling a slurry of the resin into a piece of glass tubing 7.5 inches long, 2.0 mm ID and 3.6 mm OD. This is conveniently done by using a pipet and a loose fitting glass wool plug in the tubing. Care should be taken to avoid allowing air bubbles to enter the column. If air bubbles become trapped, the column should be prepared over again. The column can exchange the equivalent of 35 mg of calcium. For the high level manifold this corresponds to about 900 samples with 200 mg/l Ca . The column should be prepared as often as necessary to assure that no more than 50% of its capacity is used up.

7.3 Allow the colorimeter, recorder and printer to warm up for 30 minutes. Pump all reagents until a stable baseline is achieved.

7.4 Analyze all working standards in duplicate at the beginning of a run to develop a standard curve. The A and B control standards are analyzed every hour to assure that the system remains properly calibrated. Since the chemistry is non-linear the 180 mg/l standard is set at 50% on the recorder using the standard calibration control on the colorimeter.

7.5 At the end of each day, the system should be washed with the buffered EDTA solution (6.4). This is done by placing the methylthymol blue line and the sodium hydroxide line in water for a few minutes and then in the buffered EDTA solution for 10 minutes. Wash the system with water for 15 minutes before shutting down.

8. Calculation

8.1 Prepare a standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with the standard curve.

9. Precision and Accuracy

9.1 In a single laboratory the estimated standard deviation, calculated from duplicate analyses of 26 surface and wastewaters at a mean concentration of 110 mg/l was ±1.6 mg/l.

9.2 The mean recovery from 24 surface and wastewaters was 102%.

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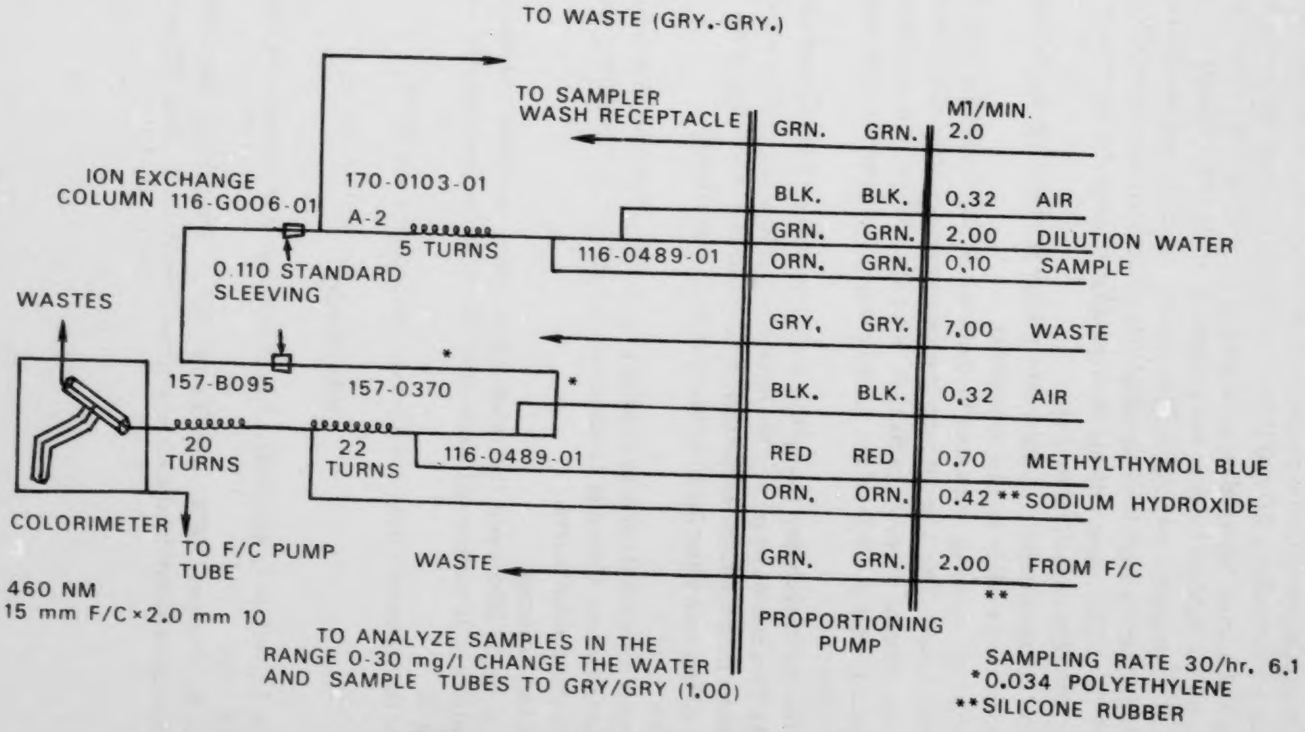
TO WASTE (GRY.-GRY.)
TO SAMPLER WASH RECEPTACLE
ION EXCHANGE COLUMN 116-G006-01
170-0103-01
A-2
5 TURNS
116-0489-01
0.110 STANDARD SLEEVING
WASTES
157-B095
157-0370
*
*
20 TURNS
22 TURNS
116-0489-01
COLORIMETER
TO F/C PUMP TUBE
WASTE
460 NM
15 mm F/C×2.0 mm 10
TO ANALYZE SAMPLES IN THE RANGE 0-30 mg/l CHANGE THE WATER AND SAMPLE TUBES TO GRY/GRY (1.00)
M1/MIN.
GRN. GRN. 2.0
BLK. BLK. 0.32 AIR
GRN. GRN. 2.00 DILUTION WATER
ORN. GRN. 0.10 SAMPLE
GRY. GRY. 7.00 WASTE
BLK. BLK. 0.32 AIR
RED RED 0.70 METHYLTHYMOL BLUE
ORN. ORN. 0.42 ** SODIUM HYDROXIDE
GRN. GRN. 2.00 FROM F/C
**
PROPORTIONING PUMP
SAMPLING RATE 30/hr. 6.1
*0.034 POLYETHYLENE
**SILICONE RUBBER

FIGURE 1 SULFATE MANIFOLD AA11

9. Precision and Accuracy

9.1 The two oil and grease methods in this manual were tested by a single laboratory (EMSL) on sewage. This method determined the oil and grease level in the sewage to be 12.6 mg/1. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 93% with a standard deviation of ±0.9 mg/1.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 515, Method 502A, (1975).
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OIL AND GREASE, TOTAL, RECOVERABLE

Method 413.1 (Gravimetric, Separatory Funnel Extraction)

STORET NO. 00556

1. Scope and Application
   - 1.1 This method includes the measurement of fluorocarbon-113 extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.
   - 1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through #2 fuel oils are completely or partially lost in the solvent removal operation.
   - 1.3 Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in fluorocarbon-113. Accordingly, recoveries of these materials will be low.
   - 1.4 The method covers the range from 5 to 1000 mg/1 of extractable material.
2. Summary of Method
   - 2.1 The sample is acidified to a low pH (< 2) and serially extracted with fluorocarbon-113 in a separatory funnel. The solvent is evaporated from the extract and the residue weighed.
3. Definitions
   - 3.1 The definition of oil and grease is based on the procedure used. The nature of the oil and/or grease, and the presence of extractable non-oily matter will influence the material measured and interpretation of results.
4. Sampling and Storage
   - 4.1 A representative sample of 1 liter volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml HCl (6.1) at the time of collection and refrigerated at 4°C.
   - 4.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.
5. Apparatus
   - 5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
   - 5.2 Vacuum pump, or other source of vacuum.
   - 5.3 Flask, boiling, 125 ml (Corning No. 4100 or equivalent).
   - 5.4 Distilling head, Claisen or equivalent.
   - 5.5 Filter paper, Whatman No. 40, 11 cm.
6. Reagents
   - 6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc. HCl and distilled water.

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6.2 Flurocarbon-113,(1,1,2-trichloro-1,2,2-trifluoroethane), b. p. 48°C.

6.3 Sodium sulfate, anhydrous crystal.

7. Procedure

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Tare a boiling flask (pre-dried in an oven at 103°C and stored in a desiccator).

7.4 Add 30 ml fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate, and filter the solvent layer into the flask through a funnel containing solvent moistened filter paper.

NOTE: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

7.5 Repeat (7.4) twice more, with additional portions of fresh solvent, combining all solvent in the boiling flask.

7.6 Rinse the tip of the separatory funnel, the filter paper, and then the funnel with a total of 10–20 ml solvent and collect the rinsings in the flask.

7.7 Connect the boiling flask to the distilling head and evaporate the solvent by immersing the lower half of the flask in water at 70°C. Collect the solvent for reuse. A solvent blank should accompany each set of samples.

7.8 When the temperature in the distilling head reaches 50°C or the flask appears dry remove the distilling head. Sweep out the flask for 15 seconds with air to remove solvent vapor by inserting a glass tube connected to a vacuum source. Immediately remove the flask from the heat source and wipe the outside to remove excess moisture and fingerprints.

7.9 Cool the boiling flask in a desiccator for 30 minutes and weigh.

8. Calculation

8.1 mg/l total oil and grease $= \frac{R - B}{V}$

where:

R = residue, gross weight of extraction flask minus the tare weight, in milligrams.

B = blank determination, residue of equivalent volume of extraction solvent, in milligrams.

V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

SULFATE

Method 375.3 (Gravimetric)

STORET NO. Total 00945

1. Scope and Application
   1.1 This method is applicable to drinking, surface and saline water, domestic and industrial wastes.
   1.2 This method is the most accurate method for sulfate concentrations above 10 mg/1. Therefore, it should be used whenever results of the greatest accuracy are required.
2. Summary of Method
   2.1 Sulfate is precipitated as barium sulfate in a hydrochloric acid medium by the addition of barium chloride. After a period of digestion, the precipitate is filtered, washed with hot water until free of chloride, ignited, and weighed as $BaSO_4$.
   2.2 Preserve by refrigeration at 4°C.
3. Interferences
   3.1 High results may be obtained for samples that contain suspended matter, nitrate, sulfite and silica.
   3.2 Alkali metal sulfates frequently yield low results. This is especially true of alkali hydrogen sulfates. Occlusion of alkali sulfate with barium sulfate causes the substitution of an element of lower atomic weight than barium in the precipitate. Hydrogen sulfate of alkali metal acts similarly and decomposes when heated. Heavy metals such as chromium and iron, cause low results by interfering with complete precipitation and by formation of heavy metal sulfates.
4. Apparatus
   4.1 Steam bath
   4.2 Drying oven, equipped with thermostatic control.
   4.3 Muffle furnace with heat indicator.
   4.4 Desiccator
   4.5 Analytical balance, capable of weighing to 0.1 mg.
   4.6 Filter paper, acid-washed, ashless hard-finish filter paper sufficiently retentive for fine precipitates.
5. Reagents
   5.1 Methyl red indicator solution: Dissolve 100 mg methyl red sodium salt in distilled water in a 100 ml volumetric flask and dilute to the mark with distilled water.
   5.2 Hydrochloric acid, HCl, 1+1
   5.3 Barium chloride solution: Dissolve 100 g $BaCl_2 \cdot 2H_2O$ in 1 liter of distilled water. Filter through a membrane filter or hard-finish filter paper. One ml of this reagent is capable of precipitating approximately 40 mg SO_4.

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5.4 Silver nitrate-nitric acid reagent: Dissolve 8.5 g $AgNO_3$ and 0.5 ml conc. HNO_3 in 500 ml distilled water.

6. Procedure

6.1 Removal of silica: If silica concentration is greater than 25 mg/l

6.1.1 Evaporate sample nearly to dryness in a platinum dish on a steam bath.

6.1.2 Add 1 ml HCl solution (5.2), tilt dish and rotate until acid contacts all of the residue.

6.1.3 Continue evaporation to dryness.

6.1.4 Complete drying in an oven at 180°C.

6.1.5 If organic matter present, char over a flame.

6.1.6 Moisten with 2 ml distilled water and 1 ml HCl solution (5.2).

6.1.7 Evaporate to dryness on a steam bath.

6.1.8 Add 2 ml HCl solution (5.2).

6.1.9 Take up soluble residue in hot distilled water and filter.

6.1.10 Wash the insoluble silica with several small portions of hot distilled water.

6.1.11 Combine filtrate and washings.

6.2 Precipitation of barium sulfate

6.2.1 If necessary, treat clarified sample to remove interfering agents.

6.2.2 Adjust to contain approximately 50 mg SO_4 ion in a 250 ml volume.

6.2.3 Adjust acidity with HCl solution (5.2) to pH 4.5 to 5.0, using pH meter or orange color of methyl red indicator (5.1).

6.2.4 Add an additional 1 to 2 ml HCl solution (5.2).

6.2.5 For lower concentrations of sulfate ion fix the total volume at 150 ml.

6.2.6 Heat to boiling and, while stirring gently, add warm $BaCl_2$ solution (5.3) slowly, until precipitation appears to be complete; then add approximately 2 ml in excess.

6.2.7 If amount of precipitate is small, add a total of 5 ml $BaCl_2$ solution (5.3).

6.2.8 Digest the precipitate at 80 to 90°C preferably overnight but for not less than 2 hours.

6.3 Filtration and Weighing

6.3.1 Mix a little ashless filter paper pulp with the $BaSO_4$ and filter at room temperature.

6.3.2 Wash the precipitate with small portions of warm distilled water until the washings are free of chloride as indicated by testing with silver nitrate-nitric acid reagent (5.4).

6.3.3 Dry the filter and precipitate.

6.3.4 Ignite at 800°C for 1 hour. DO NOT LET THE FILTER PAPER FLAME.

6.3.5 Cool in a desiccator and weigh.

7. Calculation

$$\text{mg/l } SO_4 = \frac{\text{mg } BaSO_4 \times 411.5}{\text{ml sample}}$$

8. Precision and Accuracy

8.1 A synthetic unknown sample containing 259 mg/l sulfate, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 250 ug/l nitrite N, 1.1 mg/l nitrate N and 42.5 mg/l alkalinity (contributed by $NaHCO_3$), was analyzed in 32 laboratories by the gravimetric method, with a relative standard deviation of 4.7% and a relative error of 1.9%.

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SULFATE

Method 375.4 (Turbidimetric)

STORET NO. Total 00945

1. Scope and Application
   - 1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.
   - 1.2 The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO_4/1.
   - 1.3 The minimum detectable limit is approximately 1 mg/1 sulfate.
2. Summary of Method
   - 2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer or spectrophotometer and compared to a curve prepared from standard sulfate solutions.
   - 2.2 Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.
   - 2.3 Silica in concentrations over 500 mg/1 will interfere.
3. Comments
   - 3.1 Proprietary reagents, such as Hach Sulfaver or equivalent, are acceptable.
   - 3.2 Preserve by refrigeration at 4°C.
4. Apparatus
   - 4.1 Magnetic stirrer, variable speed so that it can be held constant just below splashing. Use identical shape and size magnetic stirring bars.
   - 4.2 Photometer: one of the following which are given in order of preference.
     - 4.2.1 Nephelometer
     - 4.2.2 Spectrophotometer for use at 420 nm with light path of 4 to 5 cm.
     - 4.2.3 Filter photometer with a violet filter having a maximum near 420 nm and a light path of 4 to 5 cm.
   - 4.3 Stopwatch, if the magnetic stirrer is not equipped with an accurate timer.
   - 4.4 Measuring spoon, capacity 0.2 to 0.3 ml.
5. Reagents
   - 5.1 Conditioning reagent: Place 30 ml conc. HCl, 300 ml distilled water, 100 ml 95% ethanol or isopropanol and 75 g NaCl in solution in a container. Add 50 ml glycerol and mix.
   - 5.2 Barium chloride, $BaCl_2$, crystals, 20 to 30 mesh.
   - 5.3 Sodium carbonate solution (approximately 0.05N): Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 hours and cool in a desiccator. Weigh 2.5 ±0.2 g (to the nearest mg), transfer to a 1 liter volumetric flask and fill to the mark with distilled water.

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5.4 Standard sulfate solution (1.00 ml = 100 ug SO_4): Prepare by either 5.4.1 or 5.4.2.

5.4.1 Standard sulfate solution from H_2SO_4

5.4.1.1 Standard sulfuric acid, 0.1N: dilute 3.0 ml conc. H_2SO_4 to 1 liter with distilled water. Standardize versus 40.00 ml of 0.05 N Na_2CO_3 solution (5.3) with about 60 ml distilled water by titrating potentiometrically to pH about 5. Lift electrodes and rinse into beaker. Boil gently for 3–5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1 liter
B = ml Na_2CO_3 solution
C = ml acid used to inflection point

5.4.1.2 Standard acid, 0.02 N: Dilute appropriate amount of standard acid, 0.1 N (5.4.1.1) to 1 liter (200.00 ml if 0.1000 N). Check by standardization versus 15 ml of 0.05 N Na_2CO_3 solution (5.3).

5.4.1.3 Place 10.41 ml standard sulfuric acid, 0.02 N (5.4.1.2) in a 100 ml volumetric and dilute to the mark.

5.4.2 Standard sulfate solution from Na_2SO_4: Dissolve 147.9 mg anhydrous Na_2SO_4 in distilled water in a 1 liter volumetric flask and dilute to the mark with distilled water.

6. Procedure

6.1 Formation of barium sulfate turbidity

6.1.1 Place 100 ml sample, or a suitable portion diluted to 100 ml, into a 250 Erlenmeyer flask.

6.1.2 Add exactly 5.0 ml conditioning reagent (5.1).

6.1.3 Mix in the stirring apparatus.

6.1.4 While the solution is being stirred, add a measuring spoonful of $BaCl_2$ crystals (5.2) and begin timing immediately.

6.1.5 Stir exactly 1.0 minutes at constant speed.

6.2 Measurement of barium sulfate turbidity

6.2.1 Immediately after the stirring period has ended, pour solution into absorbance cell.

6.2.2 Measure turbidity at 30 second intervals for 4 minutes.

6.2.3 Record the maximum reading obtained in the 4 minute period.

6.3 Preparation of calibration curve.

6.3.1 Prepare calibration curve using standard sulfate solution (5.4).

6.3.2 Space standards at 5 mg/1 increments in the 0–40 mg/1 sulfate range.

6.3.3 Above 50 mg/1 the accuracy decreases and the suspensions lose stability.

6.3.4 Check reliability of calibration curve by running a standard with every 3 or 4 samples.

6.4 Correction for sample color and turbidity.

6.4.1 Run a sample blank using the procedure 6.1 and 6.2 without the addition of barium chloride (6.1.4).

7. Calculations

7.1 Read mg SO_4 from calibration curve

$$\text{mg } SO_4/1 = \frac{\text{mg } SO_4 \times 1{,}000}{\text{ml sample}}$$

8. Precision and Accuracy

8.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as Sulfate mg/liter	Precision as Standard Deviation mg/liter	Accuracy as	
		Bias, %	Bias mg/liter
8.6	2.30	−3.72	−0.3
9.2	1.78	−8.26	−0.8
110	7.86	−3.01	−3.3
122	7.50	−3.37	−4.1
188	9.58	+0.04	+0.1
199	11.8	−1.70	−3.4

(FWPCA Method Study 1, Mineral and Physical Analyses).

8.2 A synthetic unknown sample containing 259 mg/1 sulfate, 108 mg/1 Ca, 82 mg/1 Mg, 3.1 mg/1 K, 19.9 mg/1 Na, 241 mg/1 chloride, 0.250 mg/1 nitrite N, 1.1 mg/1 nitrate N, and 42.5 mg/1 total alkalinity (contributed by $NaHCO_3$) was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D516–68, Method B, p 430 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 496, Method 427C, (1975).

SULFIDE

Method 376.1 (Titrimetric, Iodine)

STORET NO. Total 00745
Dissolved 00746

1. Scope and Application
   1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes.
   1.2 Acid insoluble sulfides are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class).
   1.3 This method is suitable for the measurement of sulfide in concentrations above 1 mg/1.
2. Summary of Method
   2.1 Excess iodine is added to a sample which may or may not have been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is backtitrated with sodium thiosulfate or phenylarsine oxide.
3. Comments
   3.1 Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances will give high results.
   3.2 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form.
   3.3 If the sample is not preserved with zinc acetate and NaOH, the analysis must be started immediately. Similarly, the measurement of dissolved sulfides mut also be commenced immediately.
4. Apparatus: Ordinary laboratory glassware.
5. Reagents
   5.1 Hydrochloric acid, HCl, 6 N
   5.2 Standard iodine solution, 0.0250 N: Dissolve 20 to 25 g KI in a little water in a liter volumetric and add 3.2 g iodine. Allow to dissolve. Dilute to 1 liter and standardize against 0.0250 N sodium thiosulfate or phenylarsine oxide using a starch indicator.
   5.3 Phenylarsine oxide 0.0250 N: commercially available.
   5.4 Starch indicator: commercially available.
   5.5 Procedure for standardization (see Residual Chlorine–iodometric titration Method 330.3, section 5.15).

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6. Procedure

6.1 Unprecipitated sample

6.1.1 Place a known amount of standard iodine solution (5.2) into a 500 ml flask. The amount should be estimated to be in excess of the amount of sulfide expected.

6.1.2 Add distilled water, if necessary, to bring the volume to approximately 20 ml.

6.1.3 Add 2 ml of 6 N HCl (5.1).

6.1.4 Pipet 200 ml of sample into the flask, keeping the tip of the pipet below the surface of the sample.

6.1.5 If the iodine color disappears, add more iodine until the color remains. Record the total number of milliliters of standard iodine used in performing steps 6.1.1 and 6.1.5.

6.1.6 Titrate with the reducing solution (0.0250 N sodium thiosulfate or 0.0250 N phenylarsine oxide solution (5.3)) using a starch indicator (5.4) until the blue color disappears. Record the number of milliliters used.

6.2 Precipitated samples

6.2.1 Add the reagents to the sample in the original bottle. Perform steps 6.1.1, 6.1.3, 6.1.5, and 6.1.6.

6.3 Dewatered samples

6.3.1 Return the glass fibre filter paper which contains the sample to the original bottle. Add 200 ml distilled water. Perform steps 6.1.1, 6.1.3, 6.1.5, and 6.1.6.

6.3.2 The calculations (7) should be based on the volume of original sample put through the filter.

7. Calculations

7.1 One ml of 0.0250 N standard iodine solution (5.2) reacts with 0.4 mg of sulfide present in the titration vessel.

7.2 Use the formula

$$\text{mg/l sulfide} = \frac{400\,(A - B)}{\text{ml sample}}$$

where:

A = ml of 0.0250 N standard iodine solution (5.2)
B = ml of 0.0250N standard reducing sodium thosulfate or phenylarsine oxide) solution (5.3).

8. Precision and Accuracy

8.1 Precision and accuracy for this method have not been determined.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 505, Method 428D, (1975).

SULFIDE

Method 376.2 (Colorimetric, Methylene Blue)

STORET NO. Total 00745
Dissolved 00746

1. Scope and Application
   1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes.
   1.2 Acid insoluble sulfides are not measured by this method. Copper sulfide is the only common sulfide in this class.
   1.3 The method is suitable for the measurement of sulfide in concentrations up to 20 mg/1.
2. Summary of Method
   2.1 Sulfide reacts with dimethyl-p-phenylenediamine (p-aminodimethyl aniline) in the presence of ferric chloride to produce methylene blue, a dye which is measured at a wavelength maximum of 625 nm.
3. Comments
   3.1 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form. Dissolved oxygen should not be present in any water used to dilute standards.
   3.2 The analysis must be started immediately.
   3.3 Color and turbidity may interfere with observations of color or with photometric readings.
4. Apparatus
   4.1 Matched test tubes, approximately 125 mm long and 15 mm O.D.
   4.2 Droppers, delivering 20 drops/ml. To obtain uniform drops, hold dropper in vertical position and allow drops to form slowly.
   4.3 Photometer, use either 4.3.1 or 4.3.2.
      4.3.1 Spectrophotometer, for use at 625 nm with cells of 1 cm and 10 cm light path.
      4.3.2 Filter photometer, with filter providing transmittance near 625 nm.
5. Reagents
   5.1 Amino-sulfuric acid stock solution: Dissolve 27 g N,N-dimethyl-p-phenylenediamine oxalate (p-aminodimethylaniline) in a cold mixture of 50 ml conc. H_2SO_4 and 20 ml distilled water in a 100 ml volumetric flask. Cool and dilute to the mark. If dark discard and purchase fresh reagent. Store in dark glass bottle.
   5.2 Amino-sulfuric acid reagent: Dissolve 25 ml amino-sulfuric acid stock solution (5.1) with 975 ml of 1+1 H_2SO_4 (5.4). Store in a dark glass bottle. This solution should be clear.
   5.3 Ferric chloride solution: Dissolve 100 g $FeCl_3 \cdot 6H_2O$ in 40 ml distilled water.

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5.4 Sulfuric acid solution, H_2SO_4, 1+1

5.5 Diammonium hydrogen phosphate solution: Dissolve 400 g $(NH_4)_2HPO_4$ in 800 ml distilled water.

5.6 Methylene blue solution I: Dissolve 1.0 g of methylene blue in distilled water in a 1 liter volumetric flask and dilute to the mark. Use U.S.P. grade or one certified by the Biological Stain Commission. The dye content reported on the label should be 84% or more. Standardize (5.8) against sulfide solutions of known strength and adjust concentration so that 0.05 ml (1 drop) equals 1.0 mg/l sulfide.

5.7 Methylene blue solution II: Dilute 10.00 ml of adjusted methylene blue solution I (5.6) to 100 ml with distilled water in a volumetric flask.

5.8 Standardization of methylene blue I solution:

5.8.1 Place several grams of clean, washed crystals of sodium sulfide $Na_2S \cdot 9H_2O$ in a small beaker.

5.8.2 Add somewhat less than enough water to cover the crystals.

5.8.3 Stir occasionally for a few minutes. Pour the solution into another vessel. This reacts slowly with oxygen but the change is insignificnat over a few hours. Make the solution daily.

5.8.4 To 1 liter of distilled water add 1 drop of solution and mix.

5.8.5 Immediately determine the sulfide concentration by the methylene blue procedure (6) and by the titrimetric iodide procedure (Method 376.1, this manual).

5.8.6 Repeat using more than one drop of sulfide solution or less water until at least five tests have been made in the range of 1 to 8 mg/l sulfide.

5.8.7 Calculate the average percent error of the methylene blue procedure (6) as compared to the titrimetric iodide procedure (Method 376.1).

5.8.8 Adjust by dilution or by adding more dye to methylene blue solution I (5.6).

6. Procedure

6.1 Color development

6.1.1 Transfer 7.5 ml of sample to each of two matched test tubes using a special wide tipped pipet or filling to a mark on the test tubes.

6.1.2 To tube A add 0.5 ml amine-sulfuric acid reagent (5.2) and 0.15 ml (3 drops) $FeCl_3$ solution (5.3).

6.1.3 Mix immediately by inverting the tube only once.

6.1.4 To tube B add 0.5 ml 1+1 H_2SO_4 (5.4) and 0.15 ml (3 drops) $FeCl_3$ solution (5.3) and mix.

6.1.5 Color will develop in tube A in the presence of sulfide. Color development is usually complete in about 1 minute, but a longer time is often required for the fading of the initial pink color.

6.1.6 Wait 3 to 5 minutes.

6.1.7 Add 1.6 ml $(NH_4)_2HPO_4$ solution (5.5) to each tube.

6.1.8 Wait 3 to 5 minutes and make color comparisons. If zinc acetate was used wait at least 10 minutes before making comparison.

6.2 Color comparison

6.2.1 Visual

6.2.1.1 Add methylene blue solution I (5.6) and/or II (5.7) (depending on sulfide concentration and accuracy desired) dropwise to tube B (6.1.4) until the color matches that developed in the first tube.

6.2.1.2 If the concentration exceeds 20 mg/1, repeat 6.2.1.1 using a portion of the sample diluted to one tenth.

6.2.2 Photometric

6.2.2.1 Use a 1 cm cell for 0.1 to 2.0 mg/1. Use a 10 cm cell for up to 20 mg/1.

6.2.2.2 Zero instrument with portion of sample from tube B (6.1.4).

6.2.2.3 Prepare calibration curve from data obtained in methylene blue standardization (5.8), plotting concentraton obtained from titrimetric iodide procedure (Method 376.1) versus absorbance. A straight line relationship can be assumed from 0 to 1.0 mg/1.

6.2.2.4 Read the sulfide concentration from the calibration curve.

7. Calculations

7.1 Visual comparison: With methylene blue solution I (5.6), adjusted so that 0.05 ml (1 drop) = 1.0 mg/1 sulfide and a 7.5 ml sample

mg/1 sulfide = number drops methylene blue solution I (5.6) + 0.1 x [number of drops methylene blue solution II (5.7)].

7.2 Photometric: see 6.2.2.4

8. Precision and Accuracy:

8.1 The precision has not been determined. The accuracy is about ±10%.

Bibliography

1. Standard Methods for he Examination of Water and Wastewater, 14th edition, p. 503, Method 428C (1975).

SULFITE

Method 377.1 (Titrimetric)

STORET NO. 00740

1. Scope and Application

1.1 This method is applicable to drinking and surface waters, sewage and industrial wastes. The primary application has been to cooling, process and distribution water systems and boiler feedwaters to which sulfide is added in order to reduce dissolved oxygen and eliminate corrosion.

1.2 The minimum detectable limit is 2–3 mg/l SO_3.

2. Summary of Method

2.1 An acidified sample containing a starch indicator is titrated with a standard potassium iodide-iodate titrant to a faint permanent blue end point which appears when the reducing power of the sample has been completely exhausted.

3. Interferences

3.1 The temperature of the sample must be below 50°C.

3.2 Care must be taken to allow as little contact with air as possible. For example, do not filter the sample. Keep the buret tip below the surface of the sample.

3.3 Other oxidizable substances, such as organic compounds, ferrous iron and sulfide are positive interferences. Sulfide may be removed by adding 0.5g of zinc acetate and analyzing the supernatant of the settled sample.

3.4 Nitrite gives a negative interference by oxidizing sulfite when the sample is acidified; this is corrected by either using a proprietary indicator which eliminates nitrite or by adding sulfamic acid.

3.5 Copper and possibly other heavy metals catalyze the oxidation of sulfite; EDTA is used to complex metals.

3.6 A blank must be run to correct for interferences present in the reagents.

4. Apparatus

4.1 Standard laboratory glassware is used.

5. Reagents

5.1 Sulfuric acid, H_2SO_4, 1+1.

5.2 Starch indicator: Amylose, Mallinckrodt Chemical Works; Thyodene, Magnus Chemical Co. or equivalent.

5.3 Dual-Purpose Sulfite Indicator Powder: a proprietary formulation containing sulfamic acid to destroy nitrite.

5.4 Standard potassium iodide-iodate titrant, 0.0125N: Dissolve 445.8 mg anhydrous potassium iodate, KIO_3 (primary standard grade dried for several hours at 120°C), 4.25g

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KI and 310 mg $NaHCO_3$ in distilled water and dilute to 1 liter. This titrant is equivalent to 500 ug SO_3/1.00 ml.

5.5 Sulfamic Acid: Crystalline

5.6 EDTA Reagent: Dissolve 2.5g EDTA in 100 ml distilled water.

6. Procedure

6.1 Sampling

Contact with air must be minimized. If the sample temperature is greater than 50°C, it must be cooled in a special apparatus described elswhere (see Bibliography). Immediately add 1 ml of EDTA Solution (5.6) per 100 ml of sample.

6.2 Starch Indicator

6.2.1 Place 1 ml H_2SO_4 (5.1) in titration vessel.

6.2.2 Add 0.1 g sulfamic acid crystals (5.5).

6.2.3 Add 50 ml sample.

6.2.4 Add approximately 0.1 g starch indicator (5.2).

6.2.5 Titrate with potassium iodide-iodate titrant (5.4) until a faint permanent blue color develops. Keep the pipet tip below the surface of the sample. View the color change against a white background. Record the ml titrant.

6.2.6 Run a reagent blank using distilled water instead of sample (6.2.3).

6.3 Dual Purpose Sulfite Indicator Powder.

6.3.1 Place 50 ml sample in a titration vessel.

6.3.2 Add 3–4 drops phenolphthalein indicator.

6.3.3 Add sufficient scoops (1g) of indicator (5.3) to discharge the red color.

6.3.4 Titrate with potassium iodide-iodate titrant (5.4) until a faint permanent blue color develops. View the color change against a white background. Record the ml titrant.

6.3.5 Run a reagent blank using distilled water instead of sample (6.3.1).

7. Calculations

7.1 Use the formula:

$$\text{mg/l } SO_3 = \frac{A \times N \times 40{,}000}{\text{ml sample}}$$

where:

A = ml titrant (6.2.5 or 6.3.4) B = ml
B = ml titrant for the blank (6.2.6 or 6.3.5) and
N = normality of $KI\text{-}KIO_3$ titrant (5.4)

7.2 To calculate as Na_2SO_3

mg/l Na_2SO_3 = mg/l SO_3 x 1.57

8. Precision and Accuracy

8.1 Precision and accuracy data are not available at this time.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D1339–72, Method C, p 440 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 508, Method 429, (1975).

BIOCHEMICAL OXYGEN DEMAND

Method 405.1 (5 Days, 20°C)

STORET NO. 00310
Carbonaceous 80082

1. Scope and Application
   - 1.1 The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirements of municipal and industrial wastewaters. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD tests are used for the development of engineering criteria for the design of wastewater treatment plants.
   - 1.2 The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20°C for a specified time period (often 5 days). The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.
2. Summary of Method
   - 2.1 The sample of waste, or an appropriate dilution, is incubated for 5 days at 20°C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.
3. Comments
   - 3.1 Determination of dissolved oxygen in the BOD test may be made by use of either the Modified Winkler with Full-Bottle Technique or the Probe Method in this manual.
   - 3.2 Additional information relating to oxygen demanding characteristics of wastewaters can be gained by applying the Total Organic Carbon and Chemical Oxygen Demand tests (also found in this manual).
   - 3.3 The use of 60 ml incubation bottles in place of the usual 300 ml incubation bottles, in conjunction with the probe, is often convenient.
4. Precision and Accuracy
   - 4.1 Eighty-six analysts in fifty-eight laboratories analyzed natural water samples plus an exact increment of biodegradable organic compounds. At a mean value of 2.1 and 175 mg/l BOD, the standard deviation was ±0.7 and ±26 mg/l, respectively (EPA Method Research Study 3).
   - 4.2 There is no acceptable procedure for determining the accuracy of the BOD test.

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5. References

5.1 The procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 15th Edition, p. 483, Method 507 (1980).

5.2 Young, J. C., "Chemical Methods for Nitrification Control," J. Water Poll. Control Fed., 45, p. 637 (1973).

CHEMICAL OXYGEN DEMAND

Method 410.1 (Titrimetric, Mid-Level)

STORET NO. 00340

1. Scope and Application
   1.1 The Chemical Oxygen Demand (COD) method determines the quantity of oxygen required to oxidize the organic matter in a waste sample, under specific conditions of oxidizing agent, temperature, and time.
   1.2 Since the test utilizes a specific chemical oxidation the result has no definite relationship to the Biochemical Oxygen Demand (BOD) of the waste or to the Total Organic Carbon (TOC) level. The test result should be considered as an independent measurement of organic matter in the sample, rather than as a substitute for the BOD or TOC test.
   1.3 The method can be applied to domestic and industrial waste samples having an organic carbon concentration greater than 50 mg/1. For lower concentrations of carbon such as in surface water samples, the Low Level Modification should be used. When the chloride concentration of the sample exceeds 2000 mg/1, the modification for saline waters is required.
2. Summary of Method
   2.1 Organic and oxidizable inorganic substances in the sample are oxidized by potassium dichromate in 50% sulfuric acid solution at reflux temperature. Silver sulfate is used as a catalyst and mercuric sulfate is added to remove chloride interference. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as an indicator.
3. Sampling and Preservation
   3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.
   3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.
   3.3 Samples should be preserved with sulfuric acid to a pH <2 and maintained at 4°C until analysis.
4. Interferences
   4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.
      4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.
      4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.

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4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step. To minimize this loss the flask should be cooled during addition of the sulfuric acid solution.

4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine and estuarine samples.

5. Apparatus

5.1 Reflux apparatus: Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflex apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6. Reagents

6.1 Distilled water: Special precautions should be taken to insure that distilled water used in this test be low in organic matter.

6.2 Standard potassium dichromate solution (0.250 N): Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103°C for two hours, in distilled water and dilute to 1000 ml.

6.3 Sulfuric acid reagent: Conc. H_2SO_4 containing 23.5g silver sulfate, Ag_2SO_4, per 4.09kg bottle. With continuous stirring, the silver sulfate may be dissolved in about 30 minutes.

6.4 Standard ferrous ammonium sulfate (0.25 N): Dissolve 98.0 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml of conc. H_2SO_4 (6.8), cool and dilute to 1 liter. This solution must be standardized daily against standard $K_2Cr_2O_7$ solution (6.2).

6.4.1 Standardization: To approximately 200 ml of distilled water add 25.0 ml of 0.25 N $K_2Cr_2O_7$ (6.2) solution. Add 20 ml of H_2SO_4 (6.8) and cool. Titrate with ferrous ammonium sulfate (6.4) using 3 drops of ferroin indicator (6.6). The color change is sharp, going from blue-green to reddish-brown.

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)(0.25)}{\text{ml Fe } (NH_4)_2\ (SO_4)_2}$$

6.5 Mercuric sulfate: Powdered $HgSO_4$.

6.6 Phenanthroline ferrous sulfate (ferroin) indicator solution: Dissolve 1.48 g of 1–10 (ortho) phenanthroline monohydrate, together with 0.70 g of $FeSO_4 \cdot 7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

6.7 Silver sulfate: Powdered Ag_2SO_4.

6.8 Sulfuric acid (sp. gr. 1.84): Concentrated H_2SO_4.

7. Procedure

7.1 Place several boiling stones in the reflux flask, followed by 50.0 ml of sample or an aliquot diluted to 50.0 ml and 1 g of $HgSO_4$ (6.5). Add 5.0 ml conc. H_2SO_4 (6.8); swirl until the mercuric sulfate has dissolved. Place reflux flask in an ice bath and slowly add, with swirling, 25.0 ml of 0.25 N $K_2Cr_2O_7$ (6.2). Now add 70 ml of sulfuric acid-silver sulfate solution (6.3) to the cooled reflux flask, again using slow addition with swirling motion.

Caution: Care must be taken to assure that the contents of the flask are well mixed. If not, superheating may result, and the mixture may be blown out of the open end of the condenser.

7.1.1 If volatile organics are present in the sample, use an allihn condenser and add the sulfuric acid-silver sulfate solution through the condenser, while cooling the flask, to reduce loss by volatilization.

7.2 Apply heat to the flask and reflux for 2 hours. For some waste waters, the 2-hour reflux period is not necessary. The time required to give the maximum oxidation for a wastewater of constant or known composition may be determined and a shorter period of refluxing may be permissible.

7.3 Allow the flask to cool and wash down the condenser with about 25 ml of distilled water. If a round bottom flask has been used, transfer the mixture to a 500 ml Erlenmeyer flask, washing out the reflux flask 3 or 4 times with distilled water. Dilute the acid solution to about 300 ml with distilled water and allow the solution to cool to about room temperature. Add 8 to 10 drops of ferroin indicator (6.6) to the solution and titrate the excess dichromate with 0.25 N ferrous ammonium sulfate (6.4) solution to the end point. The color change will be sharp, changing from a blue-green to a reddish hue.

7.4 Blank–Simultaneously run a blank determination following the details given in (7.1) and (7.2), but using low COD water in place of sample.

8. Calculation

8.1 Calculate the COD in the sample in mg/l as follows:

$$\text{COD, mg/liter} = \frac{(A - B)N \times 8{,}000}{S}$$

where:

A = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the blank,
B = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the sample,
N = normality of the $Fe(NH_4)_2(SO_4)_2$ solution, and
S = milliliters of sample used for the test.

9. Precision and Accuracy

9.1 Eighty-six analysts in fifty-eight laboratories analyzed a distilled water solution containing oxidizable organic material equivalent to 270 mg/l COD. The standard deviation was ±17.76 mg/l COD with an accuracy as percent relative error (bias) of -4.7%. (EPA Method Research Study 3).

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 550, Method 508 (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1252–67, p 473 (1976).

CHEMICAL OXYGEN DEMAND

Method 410.2 (Titrimetric, Low Level)

STORET NO. 00335

1. Scope and Application

1.1 The scope of this modification of the Chemical Oxygen Demand (COD) test is the same as for the high level test. It is applicable to the analysis of surface waters, domestic and industrial wastes with low demand characteristics.

1.2 This method (low level) is applicable for samples having a COD in the range of 5–50 mg/l COD.

2. Summary of Method

2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate solution in 50 percent (by volume) sulfuric acid in solution. The excess dichromate is titrated with standard ferrous ammonium sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator.

3. Sampling and Preservation

3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.

3.3 Samples should be preserved with sulfuric acid to a $pH < 2$ and maintained at 4°C until analysis.

4. Interferences

4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.

4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.

4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.

4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.

4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine and estuarine samples.

5. Apparatus

5.1 Reflux apparatus: Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser

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by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6. Reagents

6.1 Distilled water: Special precautions should be taken to insure that distilled water used in this test be low in organic matter.

6.2 Standard potassium dichromate solution (0.025 N): Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103°C for two hours, in distilled water and dilute to 1000 ml. Mix this solution thoroughly then dilute 100.0 ml to 1000 ml with distilled water.

6.3 Sulfuric acid reagent: Conc. H_2SO_4 containing 23.5g silver sulfate, Ag_2SO_4, per 4.09kg bottle. (With continuous stirring, the silver sulfate may be dissolved in about 30 minutes.)

6.4 Standard ferrous ammonium sulfate (0.025 N): Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml of conc. H_2SO_4 (6.8), cool and dilute to 1 liter. Dilute 100 ml of this solution to 1 liter with distilled water. This solution must be standardized daily against $K_2Cr_2O_7$ solution.

6.4.1 Standardization: To approximately 200 ml of distilled water add 25.0 ml of 0.025 N $K_2Cr_2O_7$ (6.2) solution. Add 20 ml of H_2SO_4 (6.8) and cool. Titrate with ferrous ammonium sulfate (6.4) using 3 drops of ferroin indicator (6.6). The color change is sharp, going from blue-green to reddish-brown.

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)(0.025)}{\text{ml } Fe\,(NH_4)_2\,(SO_4)_2}$$

6.5 Mercuric sulfate : Powdered $HgSO_4$.

6.6 Phenanthroline ferrous sulfate (ferroin) indicator solution: Dissolve 1.48 g of 1–10 (ortho)phenanthroline monohydrate, together with 0.70 g of $FeSO_4 \cdot 7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

6.7 Silver sulfate : Powdered Ag_2SO_4.

6.8 Sulfuric acid (sp. gr. 1.84) : Concentrated H_2SO_4.

7. Procedure

7.1 Place several boiling stones in the reflux flask, followed by 50.0 ml of sample or an aliquot diluted to 50.0 ml and 1 g of $HgSO_4$ (6.5). Add 5.0 ml conc. H_2SO_4 (6.8); swirl until the mercuric sulfate has dissolved. Place reflux flask in an ice bath and slowly add, with swirling, 25.0 ml of 0.025 N $K_2Cr_2O_7$ (6.2). Now add 70 ml of sulfuric acid-silver sulfate solution (6.3) to the cooled reflux flask, again using slow addition with swirling motion.

Caution: Care must be taken to assure that the contents of the flask are well mixed. If not, superheating may result, and the mixture may be blown out of the open end of the condenser.

7.1.1 If volatile organics are present in the sample, use an Allihn condenser and add the sulfuric acid-silver sulfate solution through the condenser, while cooling the flask, to reduce loss by volatilization.

7.2 Apply heat to the flask and reflux for 2 hours. For some waste waters, the 2-hour reflux period is not necessary. The time required to give the maximum oxidation for a wastewater of constant or known composition may be determined and a shorter period of refluxing may be permissible.

7.3 Allow the flask to cool and wash down the condenser with about 25 ml of distilled water. If a round bottom flask has been used, transfer the mixture to a 500 ml Erlenmeyer flask, washing out the reflux flask 3 or 4 times with distilled water. Dilute the acid solution to about 300 ml with distilled water and allow the solution to cool to about room temperature. Add 8 to 10 drops of ferroin indicator (6.6) to the solution and titrate the excess dichromate with 0.025 N ferrous ammonium sulfate (6.4) solution to the end point. The color change will be sharp, changing from a blue-green to a reddish hue.

7.4 Blank—Simultaneously run a blank determination following the details given in (7.1) and (7.2), but using low COD water in place of sample.

8. Calculation

8.1 Calculate the COD in the sample in mg/1 as follows:

$$\text{COD, mg/1} = \frac{(A - B)N \times 8{,}000}{S}$$

where:

A = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the blank,
B = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the sample,
N = normality of the $Fe(NH_4)_2(SO_4)_2$ solution, and
S = milliliters of sample used for the test.

9. Precision and Accuracy

9.1 Eighty-six analysts in fifty-eight laboratories analyzed a distilled water solution containing oxidizable organic material equivalent to 12.3 mg/1 COD. The standard deviation was ±4.15 mg/1 COD with an accuracy as percent relative error (bias) of 0.3%. (EPA Method Research Study 3.)

CHEMICAL OXYGEN DEMAND

Method 410.3 (Titrimetric, High Level for Saline Waters)

STORET NO. 00340

1. Scope and Application
   1.1 When the chloride level exceeds 1000 mg/1 the minimum accepted value for the COD will be 250 mg/1. COD levels which fall below this value are highly questionable because of the high chloride correction which must be made.
2. Summary of Method
   2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate solution in 50 percent (by volume) sulfuric acid solution. The excess dichromate is titrated with standard ferrous ammonium sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator.
3. Sample Handling and Preservation
   3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.
   3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.
   3.3 Samples should be preserved with sulfuric acid to a pH < 2 and maintained at 4°C until analysis.
4. Interferences
   4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.
      4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.
      4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.
   4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.
   4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. A chloride correction is made using the procedure outlined in 7.7 of this method.
5. Apparatus
   5.1 Reflux apparatus: Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

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6. Reagents

6.1 Standard potassium dichromate solution, (0.25 N): Dissolve 12.2588 g of $K_2Cr_2O_7$, primary standard grade, previously dried for 2 hours at 103°C in water and dilute to 1000 ml.

6.2 Sulfuric acid reagent: Conc. H_2SO_4 containing 23.5 g silver sulfate, Ag_2SO_4, per 4.09kg. bottle. (With continuous stirring, the silver sulfate may be dissolved in about 30 minutes.)

6.3 Standard ferrous ammonium sulfate, 0.250 N: Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml of conc. H_2SO_4, (6.7), cool and dilute to 1 liter. This solution must be standardized against the standard potassium dichromate solution (6.1) daily.

6.3.1 Standardization: Dilute 25.0 ml of standard dichromate solution (6.1) to about 250 ml with distilled water. Add 20 ml conc. sulfuric acid (6.7). Cool, then titrate with ferrous ammonium sulfate titrant (6.3), using 10 drops of ferroin indicator (6.5).

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)(0.25)}{\text{ml } Fe(NH_4)_2\,(SO_4)_2}$$

6.4 Mercuric sulfate : Powdered $HgSO_4$.

6.5 Phenanthroline ferrous sulfate (ferroin) indicator solution: Dissolve 1.48 g of 1–10-(ortho) phenanthroline monohydrate, together with 0.70 g of $FeSO_4 \cdot 7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

6.6 Silver sulfate : Powdered Ag_2SO_4.

6.7 Sulfuric acid (sp. gr. 1.84) : Concentrated H_2SO_4.

7. Procedure

7.1 Pipet a 50.0 ml aliquot of sample not to exceed 800 mg/1 of COD into a 500 ml, flat bottom, Erlenmeyer flask. Add $HgSO_4$ (6.4) in the ratio of 10 mg to 1 mg chloride, based upon the mg of chloride in the sample aliquot and 5 ml of sulfuric acid (6.7). Swirl until all the mercuric sulfate has dissolved. Add 25.0 ml of 0.25N $K_2Cr_2O_7$ (6.1). Carefully add 70 ml of sulfuric acid-silver sulfate solution (6.2) and gently swirl until the solution is thoroughly mixed. Glass beads should be added to the reflux mixture to prevent bumping, which can be severe and dangerous.

Caution: The reflux mixture must be thoroughly mixed before heat is applied. If this is not done, local heating occurs in the bottom of the flask, and the mixture may be blown out of the condenser.

7.1.1 If volatile organics are present in the sample, use an Allihn condenser and add the sulfuric acid-silver sulfate solution through the condenser, while cooling the flask, to reduce loss by volatilization.

7.2 Attach the flask to the condenser and reflux the mixture for two hours.

7.3 Cool, and wash down the interior of the condenser with 25 ml of distilled water. Disconnect the condenser and wash the flask and condenser joint with 25 ml of distilled water so that the total volume is 350 ml. Cool to room temperature.

7.4 Titrate with standard ferrous ammonium sulfate (6.3) using 10 drops of ferroin (6.5) indicator. (This amount must not vary from blank, sample and standardization.) The color change is sharp, going from blue-green to reddish-brown and should be taken as the end point although the blue-green color may reappear within minutes.

7.5 Run a blank, using 50 ml of distilled water in place of the sample together with all reagents and subsequent treatment.

7.6 For COD values greater than 800 mg/1, a smaller aliquot of sample should be taken; however, the volume should be readjusted to 50 ml with distilled water having a chloride concentration equal to the sample.

7.7 Chloride correction(1): Prepare a standard curve of COD versus mg/1 of chloride, using sodium chloride solutions of varying concentrations following exactly the procedure outlined. The chloride interval, as a minimum should be 4000 mg/1 up to 20,000 mg/1 chloride. Lesser intervals of greater concentrations must be run as per the requirements of the data, but in no case must extrapolation be used.

8. Calculation

$$\text{mg/l COD} = \frac{[(A - B)C \times 8{,}000] - 50D}{\text{ml of sample}} \times 1.2$$

where:

A = ml $Fe(NH_4)_2(SO_4)_2$ for blank;
B = ml $Fe(NH_4)_2(SO_4)_2$ for sample;
C = normality of $Fe(NH_4)_2(SO_4)_2$;
D = chloride correction from curve (step 7.7)
1.2 = compensation factor to account for the extent of chloride oxidation which is dissimilar in systems containing organic and non-organic material.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

Bibliography

1. Burns, E. R., Marshall, C., Journal WPCF, Vol. 37, p 1716–1721 (1965).

CHEMICAL OXYGEN DEMAND

Method 410.4 (Colorimetric, Automated; Manual)

STORET NO. 00340

1. Scope and Application
   - 1.1 This method covers the determination of COD in surface waters, domestic and industrial wastes.
   - 1.2 The applicable range of the automated method is 3–900 mg/1 and the range of the manual method is 20 to 900 mg/1.
2. Summary of Method
   - 2.1 Sample, blanks and standards in sealed tubes are heated in an oven or block digestor in the presence of dichromate at 150°C. After two hours, the tubes are removed from the oven or digestor, cooled and measured spectrophotometrically at 600 nm.
3. Sample Handling and Preservation
   - 3.1 Collect the samples in glass bottles if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.
   - 3.2 Samples should be preserved with sulfuric acid to a $pH < 2$ and maintained at 4°C until analysis.
4. Interferences
   - 4.1 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chlorides.
5. Apparatus
   - 5.1 Drying oven or block digestor, 150°C
   - 5.2 Corning culture tubes, 16 x 100 mm or 25 x 150 mm with Teflon lined screw cap
   - 5.3 Spectrophotometer or Technicon AutoAnalyzer
   - 5.4 Muffle furnace, 500°C.
6. Reagents
   - 6.1 Digestion solution: Add 10.2 g $K_2Cr_2O_7$, 167 ml conc. H_2SO_4 and 33.3 g $HgSO_4$ to 500 ml of distilled water, cool and dilute to 1 liter.
   - 6.2 Catalyst solution: Add 22 g Ag_2SO_4 to a 4.09kg bottle of conc. H_2SO_4. Stir until dissolved.
   - 6.3 Sampler wash solution: Add 500 ml of conc H_2SO_4 to 500 ml of distilled water.
   - 6.4 Stock potassium acid phthalate: Dissolve 0.850 g in 800 ml of distilled water and dilute to 1 liter. 1 ml = 1 mg COD
     - 6.4.1 Prepare a series of standard solutions that cover the expected sample concentrations by diluting appropriate volumes of the stock standard.
7. Procedure
   - 7.1 Wash all culture tubes and screw caps with 20% H_2SO_4 before their first use to prevent contamination. Trace contamination may be removed from the tubes by igniting them in a muffle oven at 500°C for 1 hour.

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7.2 Automated

7.2.1 Add 2.5 ml of sample to the 16 x 100 mm tubes.

7.2.2 Add 1.5 ml of digestion solution (6.1) and mix.

7.2.3 Add 3.5 ml of catalyst solution (6.2) carefully down the side of the culture tube.

7.2.4 Cap tightly and shake to mix layers.

7.2.5 Process standards and blanks exactly as the samples.

7.2.6 Place in oven or block digestor at 150°C for two hours.

7.2.7 Cool, and place standards in sampler in order of decreasing concentration. Complete filling sampler tray with unknown samples.

7.2.8 Measure color intensity on AutoAnalyzer at 600 nm.

7.3 Manual

7.3.1 The following procedure may be used if a larger sample is desired or a spectrophotometer is used in place of an AutoAnalyzer.

7.3.2 Add 10 ml of sample to 25 x 150 mm culture tube.

7.3.3 Add 6 ml of digestion solution (6.1) and mix.

7.3.4 Add 14 ml of catalyst solution (6.2) down the side of culture tube.

7.3.5 Cap tightly and shake to mix layers.

7.3.6 Place in oven or block digestor at 150°C for 2 hours.

7.3.7 Cool, allow any precipitate to settle and measure intensity in spectrophotometer at 600 nm. Use only optically matched culture tubes or a single cell for spectrophotometric measurement.

8. Calculation

8.1 Prepare a standard curve by plotting peak height or percent transmittance against known concentrations of standards.

8.2 Compute concentration of samples by comparing sample response to standard curve.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

Bibliography

1. Jirka, A. M., and M. J. Carter, "Micro-Semi-Automated Analysis of Surface and Wastewaters for Chemical Oxygen Demand." Anal. Chem. 47:1397, (1975).

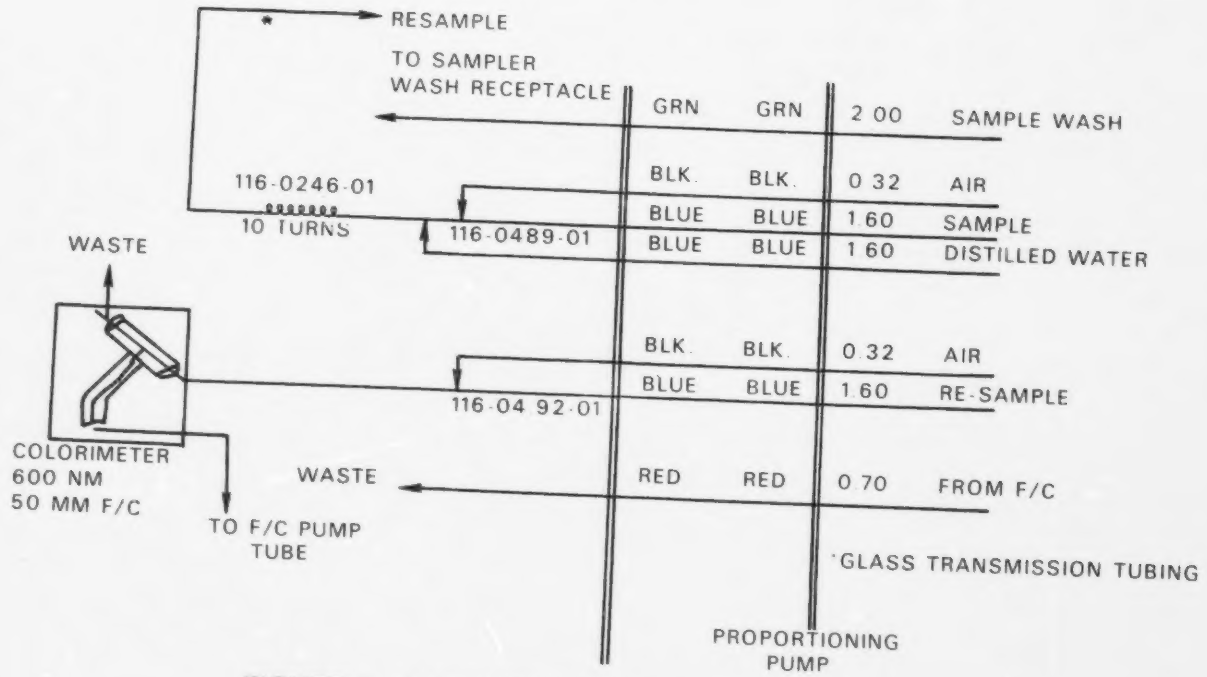
RESAMPLE
*
TO SAMPLER
WASH RECEPTACLE
GRN
GRN
2.00
SAMPLE WASH
116-0246-01
10 TURNS
BLK.
BLK.
0.32
AIR
BLUE
BLUE
1.60
SAMPLE
116-0489-01
BLUE
BLUE
1.60
DISTILLED WATER
WASTE
BLK.
BLK.
0.32
AIR
BLUE
BLUE
1.60
RE-SAMPLE
116-04 92-01
COLORIMETER
600 NM
50 MM F/C
WASTE
RED
RED
0.70
FROM F/C
TO F/C PUMP
TUBE
*GLASS TRANSMISSION TUBING
PROPORTIONING
PUMP

FIGURE 1 C O D MANIFOLD AA1 OR AA 11

OIL AND GREASE, TOTAL RECOVERABLE

Method 413.2 (Spectrophotometric, Infrared)

STORET NO. 00560

1. Scope and Application
   - 1.1 This method includes the measurement of fluorocarbon-113 extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.
   - 1.2 The method is applicable to measurement of most light petroleum fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.
   - 1.3 The method covers the range from 0.2 to 1000 mg/l of extractable material.
   - 1.4 While this method can be used to obtain an estimate of the oil and grease that would be measured gravimetrically, in many cases the estimate more accurately describes the parameter, as it will measure volatiles more effectively and is not susceptible to interferences such as extractable sulfur. It can be used with the Petroleum Hydrocarbon procedure to obtain an oil and grease value and a petroleum hydrocarbon value on the same sample.
2. Summary of Method
   - 2.1 The sample is acidified to a low pH (< 2) and extracted with fluorocarbon-113. The oil and grease is determined by comparison of the infrared absorbance of the sample extract with standards.
3. Definitions
   - 3.1 The definition of oil and grease is based on the procedure used. The source of the oil and/or grease, and the presence of extractable non-oily matter will influence the material measured and interpretation of results.
4. Sampling and Storage
   - 4.1 A representative sample of 1 liter volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml HCl (6.1) at the time of collection and refrigerated at 4°C.
   - 4.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.
5. Apparatus
   - 5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
   - 5.2 Infrared spectrophotometer, scanning. Non-scanning instruments may also be used but can be subject to positive interferences in complex chemical wastewaters.
   - 5.3 Cells, 10 mm, 50 mm, and 100 mm path length, sodium chloride or infrared grade glass.
   - 5.4 Filter paper, Whatman No. 40, 11 cm.

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6. Reagents

6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc. HCl and distilled water.

6.2 Fluorocarbon-113, (1,1,2-trichloro-1,2,2-trifluoroethane), b. p. 48°C.

6.3 Sodium sulfate, anhydrous crystal.

6.4 Calibration mixtures:

6.4.1 Reference oil: Pipet 15.0 ml n-hexadecane, 15.0 ml isooctane, and 10.0 ml chlorobenzene into a 50 ml glass stoppered bottle. Maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots.

6.4.2 Stock standard: Pipet 1.0 ml reference oil (6.4.1) into a tared 200 ml volumetric flask and immediately stopper. Weigh and dilute to volume with fluorocarbon-113.

6.4.3 Working standards: Pipet appropriate volumes of stock standard (6.4.2) into 100 ml volumetric flasks according to the cell pathlength to be used. Dilute to volume with fluorocarbon-113. Calculate concentration of standards from the stock standard.

7. Procedure

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Add 30 ml fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate.

7.4 Filter the solvent layer into a 100 ml volumetric flask through a funnel containing solvent-moistened filter paper.

NOTE: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

7.5 Repeat (7.3 and 7.4) twice more with 30 ml portions of fresh solvent, combining all solvent in the volumetric flask.

7.6 Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 5–10 ml fluorocarbon-113 and collect the rinsings in the flask. Dilute the extract to 100 ml, and stopper the flask.

7.7 Select appropriate working standards and cell pathlength according to the following table of approximate working ranges:

Pathlength	Range
10 mm	2–40 mg
50 mm	0.4–8 mg
100 mm	0.1–4 mg

7.8 Scan standards and samples from 3200 cm^{-1} to 2700 cm^{-1} with fluorocarbon-113 in the reference beam and record the results on absorbance paper. The absorbances of samples and standards are measured by constructing a straight baseline over the range of the scan and measuring the absorbance of the peak maximum at 2930 cm^{-1} and subtracting the baseline absorbance at that point. For an example of a typical oil spectrum and baseline construction, see Gruenfeld(3). Non-scanning instruments should be operated according to manufacturer's instructions, although calibration must be performed using the standards described above (6.4). If the absorbance exceeds 0.8 for a sample, select a shorter pathlength or dilute as required.

7.9 Use a calibration plot of absorbance vs. mg oil prepared from the standards to determine the mg oil in the sample solution.

8. Calculation

8.1 mg/1 total oil and grease $= \frac{R \times D}{V}$

where:

R = oil in solution, determined from calibration plot, in milligrams.
D = extract dilution factor, if used.
V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

9. Precision and Accuracy

9.1 The two oil and grease methods in this manual were tested by a single laboratory (EMSL) on sewage. This method determined the oil and grease level in the sewage to be 17.5 mg/1. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 99% with a standard deviation of ±1.4 mg/1.

Bibliography

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3. Gruenfeld, M., "Extraction of Dispersed Oils from Water for Quantitative Analysis by Infrared Spectroscopy", Environ. Sci. Technol. 7, 636 (1973).

ORGANIC CARBON, TOTAL

Method 415.1 (Combustion or Oxidation)

STORET NO. Total 00680
Dissolved 00681

1. Scope and Application
   - 1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
   - 1.2 The method is most applicable to measurement of organic carbon above 1 mg/1.
2. Summary of Method
   - 2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.
3. Definitions
   - 3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
     - A) soluble, nonvolatile organic carbon; for instance, natural sugars.
     - B) soluble, volatile organic carbon; for instance, mercaptans.
     - C) insoluble, partially volatile carbon; for instance, oils.
     - D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
     - E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
   - 3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

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4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples. **NOTE 1:** A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified ($pH \leq 2$) with HCl or H_2SO_4.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior.

7. Reagents

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.

NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as	
		Bias, %	Bias, mg/liter
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

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2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

United States
Environmental Protection
Agency

Environmental Monitoring and
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Research and Development

Test Method

Organic Carbon, Total (low level) (UV promoted, persulfate oxidation)—Method 415.2

1. Scope and Application

1.1 This method covers the determination of total organic carbon in drinking water and other waters subject to the limitations in 1.3 and 5.1.

1.2 This instrument is designed for a two-step operation to distinguish between purgeable and nonpurgeable organic carbon. These separate values are not pertinent to this method.

1.3 This method is applicable only to the carbonaceous matter which is either soluble or has a particle size of 0.2 mm or less.

1.4 The applicable range is from approximately 50 µg/L to 10 mg/L. Higher concentrations may be determined by sample dilution.

2. Summary of Method

A sample is combined with 1 mL of acidified persulfate reagent and placed in a sparger. The sample is purged with helium which transfers inorganic CO_2 and purgeable organics to a CO_2 scrubber. The CO_2 is removed with at least 99.9% efficiency with a 2.5-minute purge. The purgeable organics proceed through a reduction system where the gas stream is joined by hydrogen and passed over a nickel catalyst which converts the purgeable organic carbon to methane. The methane is measured by a flame ionization detector. The detector signal is integrated and displayed as the concentration of purgeable organic carbon.

The sample is then transferred to a quartz ultraviolet reaction coil where the nonpurgeable organics are subjected to intense ultraviolet illumination in the presence of the acidified persulfate reagent. The nonpurgeables are converted to CO_2 and transferred to a second sparger where a helium purge transfers the CO_2 to the reduction system and into the detector. The signal is integrated, added to the purgeable organic carbon value, and displayed as the concentration of total organic carbon.

3. Definitions

3.1. Total organic carbon measured by this procedure is the sum of the purgeable organic carbon and the nonpurgeable organic carbon as defined in 3.2 and 3.3.

3.2 Purgeable organic carbon is the organic carbon matter that is transferred to the gas phase when the sample is purged with helium and which passes through the CO_2 scrubber. The definition is instrument-condition dependent.

3.3 Nonpurgeable organic carbon is defined as that which remains after removal of the purgeable organic carbon from the sample containing acidified persulfate reagent and which is converted to CO_2 under the instrument conditions.

3.4 The system blank is the value obtained in 8.2 for an irradiated, recirculated reagent distilled water sample.

4. Sample Handling and Preservation

4.1 Sampling and storage of samples must be done in glass bottles. Caution: Do not leave any headspace in the sample bottle as this may contribute to loss of purgeable organics.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 When analysis cannot be performed within two hours from time of sampling, the sample should be acidified to pH 2 with H_2SO_4. Note: HCl should not be used because it is converted to chlorine during the analysis. This causes damage to the instrument.

5. Interferences

5.1 If a sample is homogenized to reduce the size of the particulate matter, the homogenizing may cause loss of purgeable organic carbon, thus yielding erroneously low results.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: A household blender or similar device that will reduce particles in the sample to less than 0.2 mm.

6.2 Apparatus for Total Organic Carbon: The essential components for the apparatus used in this method are: A sparge assembly, flow switching valves, a pyrolysis furnace, quartz ultraviolet reactor coil, reducing column, flame ionization detector, electrometer and integrator. This method is based on the Dohrmann Envirotech DC-54 Carbon Analyzer. Other instruments having similar performance characteristics may be used.

6.3 Sampling Devices: Any apparatus that will reliably transfer 10 mL of sample to the sparger. A 50 mL glass syringe is recommended when analyzing samples with easily purgeable organics so as to minimize losses.

7. Reagents

7.1 Reagent Distilled Water: Distilled water used in preparation of standards and for dilution of samples should be ultra-pure to reduce the magnitude of the blank. Carbon dioxide-free, double distilled water is recommended. The water should be distilled from permanganate or be obtained from a system involving distillation and carbon treatment. The reagent distilled water value must be compared to a system blank determined on a recirculated distilled water sample. The total organic carbon value of the reagent distilled water should be less than 60 μg/L. Purgeable organic carbon values of the reagent distilled water should be less than 4 μg/L.

7.2 Potassium hydrogen phthalate, stock solution, 500 mg carbon/liter: Dissolve 1.063 g of potassium hydrogen phthalate (Primary Standard Grade) in reagent distilled water (7.1) and dilute to 1 liter.

7.3 Potassium hydrogen phthalate (2 mg/L): Pipet 4 mL of potassium hydrogen phthalate stock solution (7.2) into a one liter volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.4 Potassium hydrogen phthalate (5 mg/L): Pipet 1 mL of potassium hydrogen phthalate stock solution (7.2) into a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.5 Potassium hydrogen phthalate (10 mg/L): Pipet 2 mL of potassium hydrogen phthalate stock solution (7.2) into a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.6 Acidified Persulfate Reagent: Place 100 mL of reagent distilled water (7.1) in a container. Add 5 g of potassium persulfate. Add 5 g (3 mL) of concentrated (85%) phosphoric acid.

7.7 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Place 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate in a 100 mL volumetric flask. Dissolve with reagent distilled water (7.1) and dilute to the mark.

7.8 Carbonate-bicarbonate, standard solution 50 mg/L: Place 5 ml of the carbonate-bicarbonate stock solution in a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

8. Procedure

8.1 Allow at least 30 minutes warm-up time. Leave instrument console on continuously when in daily use, except for the ultraviolet light source, which should be turned off when not in use for more than a few hours.

8.2 Adjust all gas flows, temperatures and cycle times to manufacturer's specifications. Perform the "System Cleanup and Calibration" procedure in the manufacturer's specifications each day. Recirculate a sample of irradiated distilled water until two consecutive readings within 10% of each other are obtained. Record the last value for the system blank. This value is a function of the total instrument operation and should not vary significantly from previous runs. Reasons for significant changes in the value should be identified.

8.3 Check the effectiveness of the CO_2 scrubber by analyzing the carbonate-bicarbonate standard solution(7.8). Add 1 mL of acidified persulfate reagent (7.6) to 50 mL of the solution. Transfer 10 mL of the solution-with-reagent to the first sparger and start the analysis cycle. No response, or a very minor reading, should be obtained from this solution.

8.4 Add 1 mL of acidified persulfate reagent (7.6) to 50 mL of reagent distilled water (7.1) blank, standards 7.3, 7.4, and 7.5 and the samples.

8.5 Calibrate the analyzer as follows:

8.5.1 Run the reagent distilled water (7.1) and 5.0 mg/L standard (7.4): Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analysis cycle

Record the meter reading (see 9.1) of the final carbon value for each of the reagent distilled water (7.1) and the standard (7.4).

If the meter reading is more than 25% above or below the calculated value of standard 7.4, reanalyze the standard and set the calibration within 25% (8.5.4), reanalyze the system blank, and then begin 8.5.1 again. If the meter reading (see 9.1) is within 25% of the calculated value, continue to next step. The calculated value is defined in 8.5.2.

8.5.2 Calculate the factor for the deviation of the instrument reading (see 9.1) for the standard (7.4) from the calculated value by:

$$\frac{\text{standard reading - calculated value}}{\text{calculated value}} = \text{FACTOR}$$

where the calculated value is that value obtained by using the weight of potassium hydrogen phthalate and does not include the carbon contributed by the reagent distilled water (7.1) with which it has been diluted.

8.5.3 Calculate the adjusted reading by:
calculated value + (RDW - (FACTOR X RDW)) = ADJUSTED READING.
where RDW = mean reagent distilled water (7.1) value.

8.5.4 Push in CALIBRATE button after READY light comes on and adjust the SPAN control to the ADJUSTED READING calculated in 8.5.3.

8.6 Analyze the standards 7.3 and 7.5 in order to check the linearity of the instrument at least once each day:

Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analyzer cycle

Record the meter reading (see 9.1) of the final carbon value for each of the standards 7.3 and 7.5.

The range of concentration used for calibrating the instrument and checking the linearity of the instrument should be ascertained from a knowledge of the range of concentrations expected from the samples. Standards for lower ranges can be prepared by diluting standards 7.2, 7.3, and 7.4.

8.7 Analyze the samples. Transfer 10 mL of sample with reagent to the first sparger and start the analysis cycle.

Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analyzer cycle

Record the meter reading (see 9.1) of the final carbon value for each of the samples.

9. Calculations

9.1 The values are read off the final digital readout in μg/L. The system blank reading obtained in 8.2 must be subtracted from all reagent distilled water, standard and sample readings.

10. Precision and Accuracy

10.1 In a single laboratory (MERL), using raw river water, centrifuged river water, drinking water, and the effluent from a carbon column which had concentrations of 3.11, 3.10, 1.79, and 0.07 mg/L total organic carbon respectively, the standard deviations from ten replicates were ±0.13, ±0.03, ±0.02, and ±0.02 mg/L, respectively.

10.2 In a single laboratory (MERL), using potassium hydrogen phthalate in distilled water at concentrations of 5.0 and 1.0 mg/L total organic carbon, recoveries were 80% and 91%, respectively.

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PETROLEUM HYDROCARBONS, TOTAL RECOVERABLE

Method 418.1 (Spectrophotometric, Infrared)

STORET NO. 45501

1. Scope and Application
   1.1 This method is for the measurement of fluorocarbon-113 extractable petroleum hydrocarbons from surface and saline waters, industrial and domestic wastes.
   1.2 The method is applicable to measurement of light fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.
   1.3 The method is sensitive to levels of 1 mg/l and less, and may be extended to ambient monitoring.
2. Summary of Method
   2.1 The sample is acidified to a low pH (<2) and serially extracted with fluorocarbon-113 in a separatory funnel. Interferences are removed with silica gel adsorbant. Infrared analysis of the extract is performed by direct comparison with standards.
3. Definitions
   3.1 As in the case of Oil and Grease, the parameter of Petroleum Hydrocarbons is defined by the method. The measurement may be subject to interferences and the results should be evaluated accordingly.
   3.2 Oil and Grease is a measure of biodegradable animal greases and vegetable oils along with the relative non-biodegradable mineral oils. Petroleum hydrocarbons is the measure of only the mineral oils. Maximum information may be obtained using both methods to measure and characterize oil and grease of all sources.
4. Sampling and Storage
   4.1 A representative sample of 1 liter volume should be collected in a glass bottle. Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. The entire sample is consumed by this test; no other analyses may be performed using aliquots of the sample.
   4.2 A delay between sampling and analysis of greater than 4 hours requires sample preservation by the addition of 5 ml HCl (6.1). A delay of greater than 48 hours also requires refrigeration for sample preservation.
5. Apparatus
   5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
   5.2 Filter paper, Whatman No. 40, 11 cm.
   5.3 Infrared spectrophotometer, scanning or fixed wavelength, for measurement around $2950\ cm^{-1}$.
   5.4 Cells, 10 mm, 50 mm, and 100 mm pathlength, sodium chloride or infrared grade glass.
   5.5 Magnetic stirrer, with Teflon coated stirring bars.
6. Reagents
   6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc HCl and distilled water.

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6.2 Fluorocarbon-113,(1,1,2-trichloro-1,2,2-trifluroethane), b.p. 48°C.

6.3 Sodium sulfate, anhydrous crystal.

6.4 Silica gel, 60–200 mesh, Davidson Grade 950 or equivalent. Should contain 1–2% water as defined by residue test at 130°C. Adjust by overnight equilibration if needed.

6.5 Calibration mixtures:

6.5.1 Reference oil: Pipet 15.0 ml n-hexadecane, 15.0 ml isooctane, and 10.0 ml chlorobenzene into a 50 ml glass stoppered bottle. Maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots.

6.5.2 Stock standard: Pipet 1.0 ml reference oil (6.5.1) into a tared 200 ml volumetric flask and immediately stopper. Weigh and dilute to volume with fluorocarbon-113.

6.5.3 Working standards: Pipet appropriate volumes of stock standard (6.5.2) into 100 ml volumetric flasks according to the cell pathlength to be used. Dilute to volume with fluorocarbon-113. Calculate concentration of standards from the stock standard.

7. Procedure

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Add 30 ml fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate.

7.4 Filter the solvent layer through a funnel containing solvent-moistened filter paper into a 100 ml volumetric flask.

NOTE 1: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

7.5 Repeat (7.3 and 7.4) twice more with 30 ml portions of fresh solvent, combining all solvent into the volumetric flask.

7.6 Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 5–10 ml solvent and collect the rinsings in the flask. Dilute the extract to 100 ml. If the extract is known to contain greater than 100 mg of non-hydrocarbon organic material, pipet an appropriate portion of the sample to a 100 ml volumetric and dilute to volume.

7.7 Discard about 5–10 ml solution from the volumetric flask. Add 3 g silica gel (6.4) and a stirring bar; stopper the volumetric flask, and stir the solution for a minimum of 5 min on a magnetic stirrer.

7.8 Select appropriate working standards and cell pathlength according to the following table of approximate working ranges:

Pathlength	Range
10 mm	2–40 mg
50 mm	0.5–8 mg
100 mm	0.1–4 mg

Calibrate the instrument for the appropriate cells using a series of working standards (6.5.3). It is not necessary to add silica gel to the standards. Determine absorbance directly for each solution at the absorbance maximum at about 2930 cm^{-1}. Prepare a calibration plot of absorbance vs. mg petroleum hydrocarbons per 100 ml solution.

7.9 After the silica gel has settled in the sample extract, fill a clean cell with solution and determine the absorbance of the extract. If the absorbance exceeds 0.8 prepare an appropriate dilution.

NOTE 2: The possibility that the absorptive capacity of the silica gel has been exceeded can be tested at this point by adding another 3.0 g silica gel to the extract and repeating the treatment and determination.

7.10 Determine the concentration of petroleum hydrocarbons in the extract by comparing the response against the calibration plot.

8. Calculations

8.1 Calculate the petroleum hydrocarbons in the sample using the formula:

$$\text{mg/l Petroleum Hydrocarbons} = \frac{R \times D}{V}$$

where:

R = mg of Petroleum Hydrocarbons as determined from the calibration plot (7.10).
D = extract dilution factor, if used.
V = volume of sample, in liters.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

PHENOLICS, TOTAL RECOVERABLE

Method 420.1 (Spectrophotometric, Manual 4-AAP with Distillation)

STORET NO. 32730

1. Scope and Application
   1.1 This method is applicable to the analysis of drinking, surface and saline waters, domestic and industrial wastes.
   1.2 The method is capable of measuring phenolic materials at the 5 ug/1 level when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.
   1.3 The method is capable of measuring phenolic materials that contain more than 50 ug/1 in the aqueous phase (without solvent extraction) using phenol as a standard.
   1.4 It is not possible to use this method to differentiate between different kinds of phenols.
2. Summary of Method
   2.1 Phenolic materials react with 4-aminoantipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown colored antipyrine dye. The amount of color produced is a function of the concentration of phenolic material.
3. Comments
   3.1 For most samples a preliminary distillation is required to remove interfering materials.
   3.2 Color response of phenolic materials with 4-amino antipyrine is not the same for all compounds. Because phenolic type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.
4. Sample Handling and Preservation
   4.1 Biological degradation is inhibited by the addition of 1 g/1 of copper sulfate to the sample and acidification to a pH of less than 4 with phosphoric acid. The sample should be kept at 4°C and analyzed within 24 hours after collection.
5. Interference
   5.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4 with H_3PO_4 and aerating briefly by stirring and adding $CuSO_4$.
   5.2 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (7.10). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

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6. Apparatus

6.1 Distillation apparatus, all glass consisting of a 1 liter pyrex distilling apparatus with Graham condenser.

6.2 pH meter.

6.3 Spectrophotometer, for use at 460 or 510 nm.

6.4 Funnels.

6.5 Filter paper.

6.6 Membrane filters.

6.7 Separatory funnels, 500 or 1,000 ml.

6.8 Nessler tubes, short or long form.

7. Reagents

7.1 Phosphoric acid solution, 1 + 9: Dilute 10 ml of 85% H_3PO_4 to 100 ml with distilled water.

7.2 Copper sulfate solution: Dissolve 100 g $CuSO_4 \cdot 5H_2O$ in distilled water and dilute to 1 liter.

7.3 Buffer solution: Dissolve 16.9 g NH_4Cl in 143 ml conc. NH_4OH and dilute to 250 ml with distilled water. Two ml should adjust 100 ml of distillate to pH 10.

7.4 Aminoantipyrine solution: Dissolve 2 g of 4AAP in distilled water and dilute to 100 ml.

7.5 Potassium ferricyanide solution: Dissolve 8 g of $K_3Fe(CN)_6$ in distilled water and dilute to 100 ml.

7.6 Stock phenol solution: Dissolve 1.0 g phenol in freshly boiled and cooled distilled water and dilute to 1 liter. 1 ml = 1 mg phenol.

7.7 Working solution A: Dilute 10 ml stock phenol solution to 1 liter with distilled water. 1 ml = 10 *ug* phenol.

7.8 Working solution B: Dilute 100 ml of working solution A to 1000 ml with distilled water. 1 ml = 1 *ug* phenol.

7.9 Chloroform

7.10 Ferrous ammonium sulfate: Dissolve 1.1 g ferrous ammonium sulfate in 500 ml distilled water containing 1 ml conc. H_2SO_4 and dilute to 1 liter with freshly boiled and cooled distilled water.

8. Procedure

8.1 Distillation

8.1.1 Measure 500 ml sample into a beaker. Lower the pH to approximately 4 with 1 + 9 H_3PO_4 (7.1), add 5 ml $CuSO_4$ solution (7.2) and transfer to the distillation apparatus. Omit adding H_2PO_4 and $CuSO_4$ if sample was preserved as described in 4.1.

8.1.2 Distill 450 ml of sample, stop the distillation, and when boiling ceases add 50 ml of warm distilled water to the flask and resume distillation until 500 ml have been collected.

8.1.3 If the distillate is turbid, filter through a prewashed membrane filter.

8.2 Direct photometric method

8.2.1 Using working solution A (7.7), prepare the following standards in 100 ml volumetric flasks.

ml of working solution A	Conc. ug/l
0	0.0
0.5	50.0
1.0	100.0
2.0	200.0
5.0	500.0
8.0	800.0
10.0	1000.0

8.2.2 To 100 ml of distillate or an aliquot diluted to 100 ml and/or standards, add 2 ml of buffer solution (7.3) and mix. The pH of the sample and standards should be 10 ±0.2.

8.2.3 Add 2.0 ml aminoantipyrine solution (7.4) and mix.

8.2.4 Add 2.0 ml potassium ferricyanide solution (7.5) and mix.

8.2.5 After 15 minutes read absorbance at 510 nm.

8.3 Chloroform extraction method

8.3.1 Using working solution B (7.8), prepare the following standards. Standards may be prepared by pipetting the required volumes into the separatory funnels and diluting to 500 ml with distilled water.

ml of working solution B	Conc. ug/l
0.0	0.0
3.0	6.0
5.0	10.0
10.0	20.0
20.0	40.0
25.0	50.0

8.3.2 Place 500 ml of distillate or an aliquot diluted to 500 ml in a separatory funnel. The sample should not contain more than 25 *ug* phenol.

8.3.3 To sample and standards add 10 ml of buffer solution (7.3) and mix. The pH should be 10 ±0.2.

8.3.4 Add 3.0 ml aminoantipyrine solution (7.4) and mix.

8.3.5 Add 3.0 ml potassium ferricyanide solution (7.5) and mix.

8.3.6 After three minutes, extract with 25 ml of chloroform (7.9). Shake the separatory funnel at least 10 times, let $CHCl_3$ settle, shake again 10 times and let chloroform settle again. Vent chloroform fumes into hood.

8.3.7 Filter chloroform extracts through filter paper. Do not add more chloroform. Carryout filtration in a hood. Dispose of chloroform in environmentally acceptable manner.

8.3.8 Read the absorbance of the samples and standards against the blank at 460 nm.

9. Calculation

9.1 Prepare a standard curve by plotting the absorbance value of standards versus the corresponding phenol concentrations.

9.2 Obtain concentration value of sample directly from standard curve.

10. Precision and Accuracy

10.1 Using the extraction procedure for concentration of color, six laboratories analyzed samples at concentrations of 9.6, 48.3, and 93.5 ug/1. Standard deviations were ±0.99, ±3.1 and ±4.2 ug/1, respectively.

10.2 Using the direct photometric procedure, six laboratories analyzed samples at concentrations of 4.7, 48.2 and 97.0 mg/1. Standard deviations were ±0.18, ±0.48 and ±1.58 mg/1, respectively.

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PHENOLICS, TOTAL RECOVERABLE

Method 420.2 (Colorimetric, Automated 4-AAP with Distillation)

STORET NO. 32730

1. Scope and Application
   1.1 This method is applicable to the analysis of drinking, surface and saline waters, domestic and industrial wastes.
   1.2 The method is capable of measuring phenolic materials from 2 to 500 *ug/l* in the aqueous phase using phenol as a standard. The working ranges are 2 to 200 *ug/l* and 10 to 500 *ug/l*.
2. Summary of Method
   2.1 This automated method is based on the distillation of phenol and subsequent reaction of the distillate with alkaline ferricyanide and 4-aminoantipyrine to form a red complex which is measured at 505 or 520 nm. The same manifold is used with the AAI or AAII.
3. Sample Handling and Preservation
   3.1 Biological degradation is inhibited by the addition of 1 g/l of copper sulfate to the sample and acidification to a pH of less than 4 with phosphoric acid. The sample should be kept at 4°C and analyzed within 24 hours after collection.
4. Interference
   4.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4.0 with H_3PO_4 and aerating briefly by stirring and adding $CuSO_4$.
   4.2 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (6.5). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.
   4.3 Background contamination from plastic tubing and sample containers is eliminated by filling the wash receptacle by siphon (using Kel-F tubing) and using glass tubes for the samples and standards.
5. Apparatus
   5.1 Technicon AutoAnalyzer (I or II)
      5.1.1 Sampler equipped with continuous mixer.
      5.1.2 Manifold.
      5.1.3 Proportioning pump II or III.
      5.1.4 Heating bath with distillation coil.
      5.1.5 Distillation head.
      5.1.6 Colorimeter equipped with a 50 mm flow cell and 505 or 520 nm filter.
      5.1.7 Recorder.
6. Reagents
   6.1 Distillation reagent: Add 100 ml of conc. phosphoric acid (85% H_3PO_4) to 800 ml of distilled water, cool and dilute to 1 liter.

Issued 1974

6.2 Buffered potassium ferricyanide: Dissolve 2.0 g potassium ferricyanide, 3.1 g boric acid and 3.75 g potassium chloride in 800 ml of distilled water. Adjust to pH of 10.3 with 1 N sodium hydroxide (6.3) and dilute to 1 liter. Add 0.5 ml of Brij-35. Prepare fresh weekly.

6.3 Sodium hydroxide (1N): Dissolve 40 g NaOH in 500 ml of distilled water, cool and dilute to 1 liter.

6.4 4-Aminoantipyrine: Dissolve 0.65 g of 4-aminoantipyrine in 800 ml of distilled water and dilute to 1 liter. Prepare fresh each day.

6.5 Ferrous ammonium sulfate: Dissolve 1.1 g ferrous ammonium sulfate in 500 ml distilled water containing 1 ml H_2SO_4 and dilute to 1 liter with freshly boiled and cooled distilled water.

6.6 Stock phenol: Dissolve 1.00 g phenol in 500 ml of distilled water and dilute to 1000 ml. Add 1 g $CuSO_4$ and 0.5 ml conc. H_3PO_4 as preservative. 1.0 ml = 1.0 mg phenol.

6.7 Standard phenol solution A: Dilute 10.0 ml of stock phenol solution (6.6) to 1000 ml. 1.0 ml = 0.01 mg phenol.

6.8 Standard phenol solution B: Dilute 100.0 ml of standard phenol solution A (6.7) to 1000 ml with distilled water. 1.0 ml = 0.001 mg phenol.

6.9 Standard solution C: Dilute 100.0 ml of standard phenol solution B (6.8) to 1000 ml with distilled water. 1.0 ml = 0.0001 mg phenol.

6.10 Using standard solution A, B or C prepare the following standards in 100 ml volumetric flasks. Each standard should be preserved by adding 0.1 g $CuSO_4$ and 2 drops of conc. H_3PO_4 to 100.0 ml.

ml of Standard Solution	Conc. ug/l
Solution C	
1.0	1.0
2.0	2.0
3.0	3.0
5.0	5.0
Solution B	
1.0	10.0
2.0	20.0
5.0	50.0
10.0	100.0
Solution A	
2	200
3	300
5	500

7. Procedure

7.1 Set up the manifold as shown in Figures 1 or 2.

7.2 Fill the wash receptacle by siphon. Use Kel-F tubing with a fast flow (1 liter/hr).

7.3 Allow colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Use polyethylene tubing for sample line. When new tubing is used, about 2 hours may be required to obtain a stable baseline. This two hour time period may be necessary to remove the residual phenol from the tubing.

7.4 Place appropriate phenol standards in sampler in order of decreasing concentration. Complete loading of sampler tray with unknown samples, using glass tubes.

NOTE 1: If samples have not been preserved as instructed in (3.1), add 0.1 g $CuSO_4$ and 2 drops of conc. H_3PO_4 to 100 ml of sample.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of standards against concentration values. Compute concentration of samples by comparing sample peak heights with standards.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using sewage samples at concentrations of 3.8, 15, 43 and 89 *ug*/1, the standard deviations were ±0.5, ±0.6, ±0.6 and ±1.0 *ug*/1, respectively. At concentrations of 73, 146, 299 and 447 *ug*/1, the standard deviations were ±1.0, ±1.8, ±4.2 and ±5.3 *ug*/1, respectively.

9.2 In a single laboratory (EMSL), using sewage samples at concentrations of 5.3 and 82 *ug*/1, the recoveries were 78% and 98%. At concentrations of 168 and 489 *ug*/1, the recoveries were 97% and 98%, respectively.

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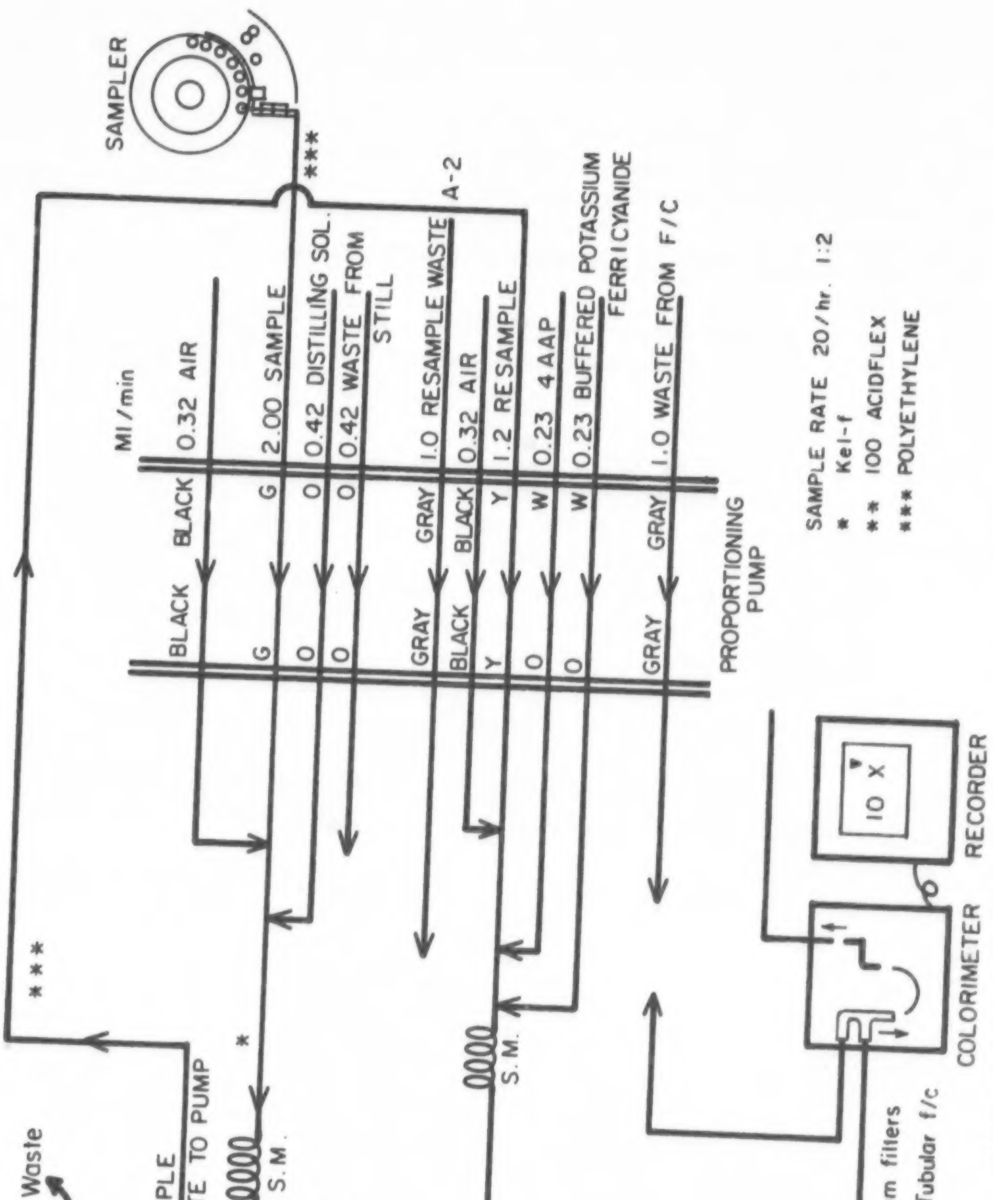
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 574, Method 510 (1975).
3. Gales, M.E. and Booth, R.L., "Automated 4 AAP Phenolic Method", AWWA 68, 540 (1976).


SAMPLER
***
A-2
Ml/min
BLACK
BLACK
0.32 AIR
G
G
2.00 SAMPLE
O
O
0.42 DISTILLING SOL.
O
O
0.42 WASTE FROM STILL
GRAY
GRAY
1.0 RESAMPLE WASTE
BLACK
BLACK
0.32 AIR
Y
Y
1.2 RESAMPLE
O
W
0.23 4 AAP
O
W
0.23 BUFFERED POTASSIUM FERRICYANIDE
GRAY
GRAY
1.0 WASTE FROM F/C
PROPORTIONING PUMP
***
*
S.M.
S.M.
To Waste
RESAMPLE WASTE TO PUMP
**
150 °C
HEATING BATH WITH DISTILLATION COIL
505 μm filters
50 mm Tubular f/c
COLORIMETER
RECORDER
10 X

SAMPLE RATE 20/hr. 1:2
* Kel-f
** 100 ACIDFLEX
*** POLYETHYLENE

FIGURE 1. PHENOL AUTO ANALYZER I

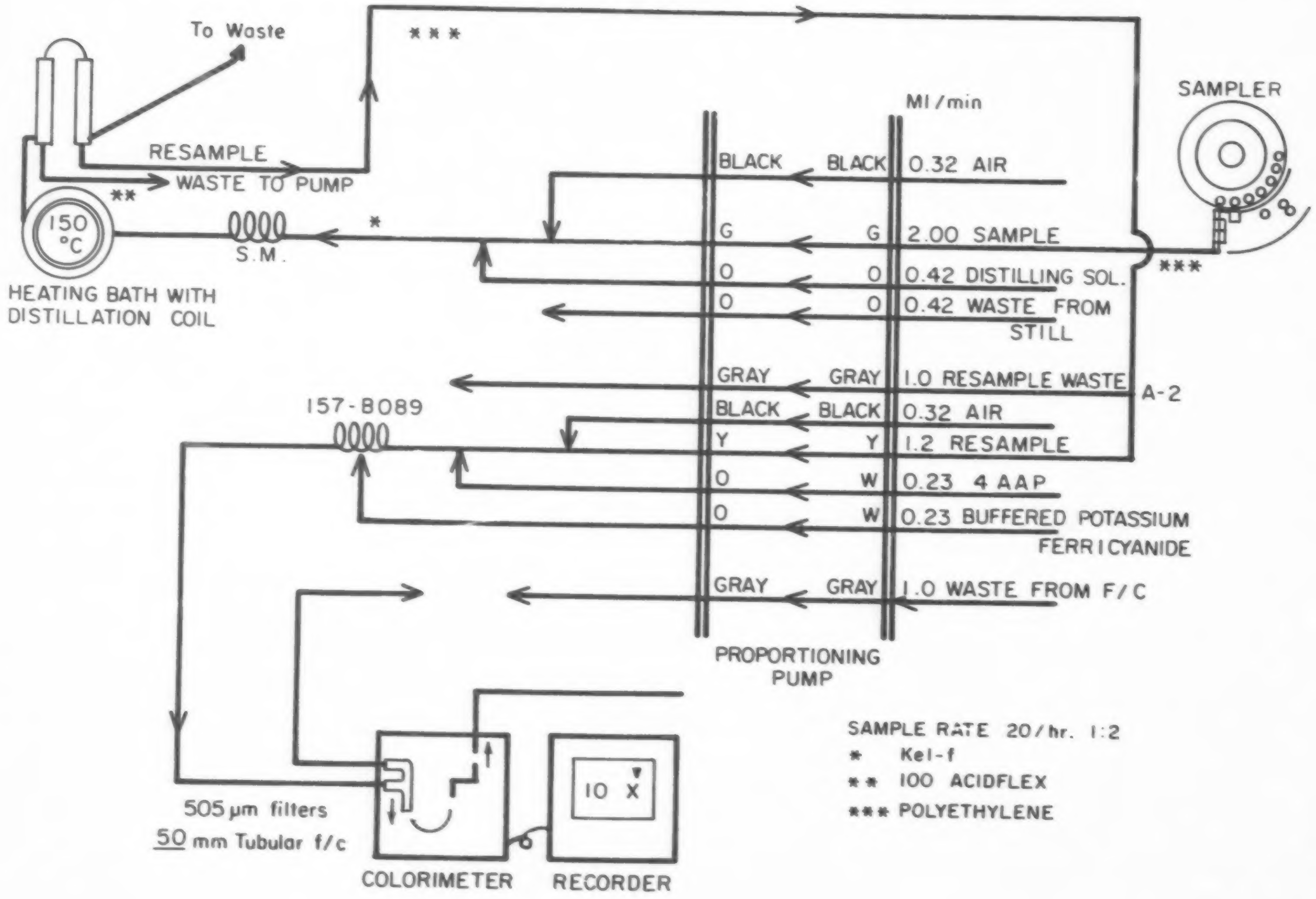

To Waste
* * *
RESAMPLE
WASTE TO PUMP
**
150 °C
S.M.
*
HEATING BATH WITH
DISTILLATION COIL
SAMPLER
Ml/min
BLACK
BLACK
0.32 AIR
G
G
2.00 SAMPLE
***
O
O
0.42 DISTILLING SOL.
O
O
0.42 WASTE FROM STILL
GRAY
GRAY
1.0 RESAMPLE WASTE
A-2
157-B089
BLACK
BLACK
0.32 AIR
Y
Y
1.2 RESAMPLE
O
W
0.23 4 AAP
O
W
0.23 BUFFERED POTASSIUM FERRICYANIDE
GRAY
GRAY
1.0 WASTE FROM F/C
PROPORTIONING PUMP
SAMPLE RATE 20/hr. 1:2
* Kel-f
** 100 ACIDFLEX
*** POLYETHYLENE
10 X
505 μm filters
50 mm Tubular f/c
COLORIMETER
RECORDER

FIGURE 2. PHENOL AUTO ANALYZER II

PHENOLICS, TOTAL RECOVERABLE

Method 420.3 (Spectrophotometric, MBTH with Distillation)

STORET NO. 32730

1. Scope and Application
    1.1 This method is applicable to the analysis of drinking, surface and saline waters, domestic and industrial wastes.
    1.2 The method is capable of measuring phenolic materials at the 2 ug/1 level when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.
    1.3 The method is capable of measuring phenolic materials that contain from 50 to 1000 ug/1 in the aqueous phase (without solvent extraction) using phenol as a standard.
    1.4 It is not possible to use this method to differentiate between different kinds of phenols.
2. Summary of Method
    2.1 This method is based on the coupling of phenol with MBTH in an acid medium using ceric ammonium sulfate as an oxidant. The coupling takes place in the p-position; if this position is occupied, the MBTH reagent will react at a free o-position. The colors obtained have maximum absorbance from 460–595 nm. For phenol and most phenolic mixtures the absorbance is 520 and 490 nm.
3. Comments
    3.1 For most samples a preliminary distillation is required to remove interfering materials.
    3.2 Color response of phenolic materials with MBTH is not the same for all compounds. Because phenolic type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.
4. Sample Handling and Preservation
    4.1 Biological degradation is inhibited by the addition of 1 g/1 of copper sulfate to the sample and acidification to a pH of less than 4 with sulfuric acid. The sample should be kept at 4°C and analyzed within 24 hours after collection.
5. Interference
    5.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4.0 with H_2SO_4 and aerating briefly by stirring and adding $CuSO_4$.
    5.2 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (6.5). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.
    5.3 Phosphate causes a precipitate to form; therefore, phosphoric acid should not be used for preservation. All glassware should be phosphate free.

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5.4 High concentrations of aldehydes may be an interference.

6. Apparatus

6.1 Distillation apparatus: All glass consisting of a 1 liter pyrex distilling apparatus with Graham condensor.

6.2 pH meter.

6.3 Spectrophotometer.

6.4 Funnels.

6.5 Filter paper.

6.6 Membrane filters.

6.7 Separatory funnels.

7. Reagents

7.1 Copper sulfate solution: Dissolve 100 g $CuSO_4 \cdot 5\ H_2O$ in distilled water and dilute to 1 liter.

7.2 Sulfuric acid, 1 N: Add 28 ml of conc. H_2SO_4 to 900 ml of distilled water, mix and dilute to 1 liter.

7.3 MBTH solution, 0.05%: Dissolve 0.1 g of 3-methyl-2-benzothiazolinone hydrazone hydrochloride in 200 ml of distilled water.

7.4 Ceric ammonium sulfate solution: Add 2.0 g of $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ and 2.0 ml of conc. H_2SO_4 to 150 ml of distilled water. After the solid has dissolved dilute to 200 ml with distilled water.

7.5 Buffer solution: Dissolve in the following order, 8 g of sodium hydroxide, 2 g EDTA (disodium salt) and 8 g boric acid in 200 ml of distilled water. Dilute to 250 ml with distilled water.

7.6 Working buffer solution: Make a working solution by mixing an appropriate volume of buffer solution (7.5) with an equal volume of ethanol.

7.7 Chloroform

7.8 Stock phenol: Dissolve 1.00 g phenol in 500 ml of distilled water and dilute to 1000 ml. Add 1 g $CuSO_4$ and 0.5 ml conc. H_2SO_4 as preservative. 1.0 ml = 1.0 mg phenol.

7.9 Standard phenol solution A: Dilute 10.0 ml of stock phenol solution (7.8) to 1000 ml. 1.0 ml = 0.01 mg phenol.

7.10 Standard phenol solution B: Dilute 100.0 ml of standard phenol solution A (7.9) to 1000 ml with distilled water. 1.0 ml = 0.001 mg phenol.

8. Procedure

8.1 Distillation

8.1.1 To 500 ml of sample add 5 ml of copper sulfate solution (7.1) and adjust the pH to approximately 4 with 1 N sulfuric acid solution (7.2).

8.1.2 Distill over 450 ml of sample, add 50 ml of warm distilled water to flask, and resume distillation until 500 ml has been collected.

8.1.3 If the distillate is turbid, filter through a prewashed membrane filter.

8.2 Concentration above 50 *ug*/1.

8.2.1 To 100 ml of distillate or an aliquot diluted to 100 ml, add 4 ml of MBTH solution (7.3).

8.2.2 After 5 minutes, add 2.5 ml of ceric ammonium sulfate solution (7.4).

8.2.3 Wait another 5 minutes and add 7 ml of working buffer solution (7.6).

8.2.4 After 15 minutes, read the absorbance at 520 nm against a reagent blank. The color is stable for 4 hours.

8.3 Concentration below 50 *u*g/1.

8.3.1 To 500 ml of distillate in a separately funnel, add 4 ml of MBTH solution (7.3).

8.3.2 After 5 minutes, add 2.5 ml of ceric ammonia sulfate solution (7.4).

8.3.3 After an additional 5 minutes, add 7 ml of working buffer solution (7.6).

8.3.4 After 15 minutes, add 25 ml of chloroform. Shake the separatory funnel at least 20 times. Allow the layer to separate, and pass the chloroform layer through filter paper.

8.3.5 Read the absorbance at 490 nm against a reagent blank.

9. Calculation

9.1 Prepare a standard curve by plotting absorbance against concentration values.

9.2 Obtain concentration value of sample directly from prepared standard curve.

10. Precision and Accuracy

10.1 Precision and accuracy data are not available at this time.

Bibliography

1. Friestad, H.O., Ott, E.E., and Gunther, F.A., "Automated Colorimetric Micro Determination of Phenol by Oxidative Coupling with 3-Methyl-2-benzothiazolinone Hydrazone", Technicon International Congress (1969).

2. Gales, M. E., "An Evaluation of the 3-Methyl-2 benzothiazolinone Hydrazone Method for the Determination of Phenols in Water and Wastewater", Analyst, 100, No. 1197, 841 (1975).

METHYLENE BLUE ACTIVE SUBSTANCES (MBAS)

Method 425.1 (Colorimetric)

STORET NO. 38260

1. Scope and Application
   1.1 This method is applicable to the measurement of methylene blue active substances (MBAS) in drinking waters, surface waters, domestic and industrial wastes. It is not applicable to measurement of surfactant-type materials in saline waters.
   1.2 It is not possible to differentiate between linear alkyl sulfonate (LAS) and alkyl benzene sulfonate (ABS) or other isomers of these types of compounds. However, LAS has essentially replaced ABS on the surfactant market so that measurable surfactant materials will probably be LAS type materials.
   1.3 The method is applicable over the range of 0.025 to 100 mg/1 LAS.
2. Summary of Method
   2.1 The dye, methylene blue, in aqueous solution reacts with anionic-type surface active materials to form a blue colored salt. The salt is extractable with chloroform and the intensity of color produced is proportional to the concentration of MBAS.
3. Comments
   3.1 Materials other than man-made surface active agents which react with methylene blue are organically bound sulfates, sulfonates, carboxylates, phosphates, phenols, cyanates, thiocyanates and some inorganic ions such as nitrates and chlorides. However, the occurrence of these materials at interference levels is relatively rare and with the exception of chlorides may generally be disregarded.
   3.2 Chlorides at concentration of about 1000 mg/1 show a positive interference but the degree of interference has not been quantified. For this reason the method is not applicable to brine samples.
   3.3 Naturally occurring organic materials that react with methylene blue are relatively insignificant. Except under highly unusual circumstances, measurements of MBAS in finished waters, surface waters and domestic sewages may be assumed to be accurate measurements of man-made surface active agents.
4. Precision and Accuracy
   4.1 On a sample of filtered river water, spiked with 2.94 mg LAS/liter, 110 analysts obtained a mean of 2.98 mg/1 with a standard deviation of ±0.272.
   4.2 On a sample of tap water spiked with 0.48 mg LAS/liter, 110 analysts obtained a mean of 0.49 mg/1 with a standard deviation of ±0.048.
   4.3 On a sample of distilled water spiked with 0.27 mg LAS/liter, 110 analysts obtained a mean of 0.24 mg/1 with a standard deviation of ±0.036.
   4.4 Analytical Reference Service, Water Surfactant No. 3, Study No. 32, (1968).

Approved for NPDES
Issued 1971

5. References

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewaters, 14th Edition, p 600, Method No. 512A (1975).

Annual Book of ASTM Standards, Part 31, "Water", Standard D 2330–68, Method A, p 494 (1976).

NTA

Method 430.1 (Colorimetric, Manual, Zinc-Zincon)

STORET NO. 00695

1. Scope and Application
   1.1 In this method NTA refers to the tri-sodium salt of nitrilotriacetic acid, $N(CH_2COONa)_3$.
   1.2 This method is applicable to surface waters in the range of 0.5–10.0 mg/l NTA.
2. Summary of Method(1)
   2.1 Zinc forms a blue-colored complex with 2 carboxy-2'-hydroxy-5'-sulfoformazylbenzene (Zincon) in a solution buffered to pH 9.2. When NTA is added, the Zinc-Zincon complex is broken which reduces the absorbance in proportion to the amount of NTA present.
3. Sample Handling and Preservation
   3.1 Samples should be analyzed as soon as possible, as NTA has been shown to be biodegradable(2).
4. Interferences
   4.1 Cations, such as calcium, magnesium, zinc, copper, iron, and manganese, complex with NTA and give a negative interference. These ions are removed by batch treating samples with ion-exchange resin. At concentrations higher than expected in typical river waters(3), only zinc, copper, and iron were not completely removed with ion-exchange treatment. Results are summarized in Table 1.

Table 1
Interference of Common Metals

		1.0 mg/l NTA	5.0 mg/l NTA
Metal	mg/l added	Recoveries	
Blank	0.0	1.1	5.5
Zinc	2.0	<0.5	0.6
Boron	5.0	1.1	5.5
Iron	5.0	0.95	4.6
Molybdenum	2.0	1.0	5.5
Manganese	4.0	1.1	5.6
Aluminum	3.0	0.85	5.2
Copper	0.5	<0.5	3.4
Strontium	5.0	1.0	5.4

   4.2 This method has not been found applicable to salt waters.

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5. Apparatus

   5.1 Shaking machine, tray type, for stirring sample-resin mixtures in 125 ml Erlenmeyer flasks.

   5.2 Photometer, suitable for measurements at 620 nm.

6. Reagents

   6.1 Sodium hydroxide, 6N: Dissolve 120 g NaOH in distilled water and dilute to 500 ml.

   6.2 Buffer: Dissolve 31 g boric acid and 37 g potassium chloride in 800 ml distilled water. Adjust pH to 9.2 with 6N NaOH (6.1). Dilute to 1 liter.

   6.3 Hydrochloric acid, 2N: Dilute 83 ml conc. HCl to 500 ml with distilled water.

   6.4 Zinc: Dissolve 0.44 g $ZnSO_4 \cdot 7H_2O$ in 100 ml 2N HCl (6.3) and dilute to 1 liter with distilled water.

   6.5 Sodium hydroxide, 1N: Dissolve 4 g NaOH in distilled water and dilute to 100 ml.

   6.6 Zinc-Zincon: Dissolve 0.13 g Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazyl benzene) in 2 ml 1N NaOH (6.5). Add 300 ml buffer (6.2). While stirring, add 15 ml Zinc solution (6.4) and dilute to 1 liter with distilled water.

   6.7 Ion-exchange resin: Dowex 50W-X8, 50–100 mesh, Na^+ form (or equivalent).

   6.8 Stock NTA solution: Dissolve 1.0700 g $N(CH_2COONa)_3 \cdot H_2O$ in distilled water and dilute to 1000 ml. 1.0 ml = 1.0 mg NTA.

7. Procedure

   7.1 Filter approximately 50 ml of well-mixed sample through a 0.45*u* membrane filter.

   7.2 Prepare a series of standards from 0.5 to 10 mg/1 NTA, including a blank of distilled water. Treat standards and blank in same manner as filtered samples.

   7.3 To a 25 ml sample in a 125 ml Erlenmeyer flask add approximately 2.5 g ion-exchange resin (6.7). Agitate sample for at least 15 minutes.

   7.4 Filter through coarse filter paper to remove resin. Pipette 15.0 ml of filtrate into a 50 ml beaker. Add 25.0 ml Zinc-Zincon (6.6) by pipette.

   7.5 Read absorbance against distilled water at 620 nm in a 1 cm or 2 cm cell.

8. Calculation

   8.1 Prepare standard curve by plotting absorbance of standards vs. NTA concentrations. Calculate concentrations of NTA, mg/1, directly from this curve.

9. Precision and Accuracy

   9.1 In a single laboratory (MDQARL), using spiked surface water samples at concentrations of 0.5, 2, 6, and 10 mg/1 NTA, standard deviations were ±0.17, ±0.14, ±0.1, and ±0.16, respectively.

   9.2 In a single laboratory (MDQARL), using spiked surface water samples at concentrations of 1.0 and 7.5 mg/1 NTA, recoveries were 120% and 103%, respectively.

Bibliography

1. Thompson, J. E., and Duthie, J. R., "The Biodegradability and Treatment of NTA", Jour. WPCF, 40, No. 2, 306 (1968).

2. Shumate, K. S. et al, "NTA Removal by Activated Sludge – Field Study", ibid., 42, No. 4, 631 (1970).

3. Kopp, J. F., and Kroner, R. C., "Trace Metals in Waters of the United States", USDI, FWPCA, DPS, 1014 Broadway, Cincinnati, Ohio 45202.

NTA

Method 430.2 (Colorimetric, Automated, Zinc-Zincon)

STORET NO. 00695

1. Scope and Application
   - 1.1 In this method, NTA refers to the tri-sodium salt of nitrilotriacetic acid, $N(CH_2COONa)_3$.
   - 1.2 This method is applicable to surface waters in the range of 0.04 to 1.0 mg/l and 0.5 to 10.0 mg/l NTA, depending on which manifold system is used. It does not apply to saline waters; a positive interference of 0.5 to 1.0 mg/l is present in sewage-type samples.
   - 1.3 Approximately 13 samples per hour can be analyzed.
2. Summary of Method(1)
   - 2.1 Zinc forms a blue-colored complex with 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene (Zincon) in a solution buffered to pH 9.2. When NTA is addd, the Zinc-Zincon complex is broken which reduces the absorbance in proportion to the amount of the NTA present.
3. Sample Handling and Preservation
   - 3.1 Samples should be analyzed as soon as possible, as NTA has been shown to be biodegradable.(2)
4. Interferences
   - 4.1 Cations, such as calcium, magnesium, zinc, copper, iron, and manganese, complex with NTA and give a negative interference. These ions are removed automatically by passing the sample through an ion-exchange column. At concentrations higher than expected in typical river waters,(3) only iron was not completely removed by this column treatment. Results, summarized in Tables 1 and 2, show that iron gives a negative interference in concentrations above 3.0 mg/l NTA.

TABLE 1

Interference of Common Metals

		Recoveries	
Metal	mg/l added	1.0 mg/l NTA	5.0 mg/l NTA
Blank	0.0	1.0	5.0
Zinc	2.0	0.9	4.9
Iron	5.0	0.8	3.8
Manganese	4.0	1.0	4.9
Copper	0.5	1.2	4.9

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TABLE 2

Effect of Iron on NTA Recovery in River Water

Iron Added mg/l	NTA Recovered, mg/l (0.5 mg/l added)
0.0	0.52
0.5	0.52
1.0	0.52
2.0	0.52
3.0	0.48
4.0	0.45
5.0	0.39

4.2 At concentration levels below 0.05 mg/1 NTA, negative peaking may occur during analyses.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I or II.

5.1.2 Manifold.

5.1.3 Proportioning pump.

5.1.4 Colorimeter equipped with 15 mm tubular flow cell and 600 or 625 nm filter.

5.1.5 Recorder

6. Reagents

6.1 Sodium hydroxide, 6N: Dissolve 120 g NaOH in distilled water and dilute to 500 ml.

6.2 Buffer: Dissolve 31 g boric acid and 37 g potassium chloride in 800 ml distilled water. Adjust pH of solution to 9.2 with 6N NaOH (6.1). Dilute to 1 liter.

6.3 Hydrochloric acid, 2N: Dilute 83 ml conc. HCl to 500 ml with distilled water.

6.4 Zinc: Dissolve 0.44 g $ZnSO_4 \cdot 7H_2O$ in 100 ml 2N HCl (6.3). Dilute to 1 liter with distilled water.

6.5 Sodium hydroxide, 1N: Dissolve 4 g NaOH in distilled water and dilute to 100 ml.

6.6 Zinc-Zincon reagent A (0.04–1.0 mg/1 NTA): Dissolve 0.065 g Zincon powder (2-carboxy-2'-hydroxy-5'-sulfoformazyl benzene) in 2 ml of 1 N NaOH (6.5). Add 300 ml buffer (6.2). Stir on a magnetic stirrer and add 7.5 ml zinc solution (6.4). Dilute to 1 liter with distilled water. This solution is stable for 12 hours.

6.7 Zinc-Zincon reagent B (0.5–10 mg/1 NTA): Dissolve 0.13 g Zincon in 2 ml 1 N NaOH (6.5). Stir on magnetic stirrer and add 300 ml buffer (6.2) and 15 ml zinc solution (6.4). Dilute to 1 liter with distilled water. Stable for 1 week.

6.8 Ion-exchange resin, H^+ form: 20–50 mesh or 30–80 mesh, Dowex 50W-XB or equivalent.

NOTE: Column is prepared by sucking a water slurry of the resin into 12 inches of 3/16-inch OD sleeving. This may be conveniently done by using a pipette and a loose-fitting glass wool plug in the sleeve.

6.9 Stock NTA solution: Dissolve 1.0700 g of $N(CH_2COONa)_3 \cdot H_2O$ in 500 ml of distilled water and dilute to 1000 ml. 1.0 ml = 1.0 mg NTA.

6.10 Working solution A: Dilute 10.0 ml of stock NTA solution to 100.0 ml with distilled water. 1.0 ml = 0.1 mg NTA. Prepare daily.

6.11 Working solution B: Dilute 10.0 ml of Solution A to 100.0 ml with distilled water. 1.0 ml = 0.01 mg NTA. Prepare daily.

6.12 Working solution C: Dilute 10.0 ml of Solution B to 100.0 ml with distilled water. 1.0 ml = 0.001 mg NTA. Prepare daily.

6.13 Prepare a series of standards by diluting suitable volumes of working solutions to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Solution C/100 ml	Conc., mg NTA/l
2	0.02
4	0.04
6	0.06
8	0.08
10	0.10
ml of Solution B/100 ml	
2	0.20
4	0.40
6	0.60
8	0.80
10	1.00
ml of Solution A/100 ml	
2	2.0
4	4.0
6	6.0
8	8.0
10	10.0

7. Procedure

7.1 Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.

7.3 Place wash water tubes in sampler in sets of two, leaving every third position vacant. Set sampling time at 1.5 minutes.

7.4 Place NTA standards in sampler. Complete filling of sample tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed NTA standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 0.1, 0.18, 0.27, and 0.44 mg/1, the standard deviations were ±0.01, ±0.004, ±0.004, and ±0.005, respectively. At concentrations of 1.3, 4.0, 5.8, and 7.4 mg/1, the standard deviations were ±0.05, ±0.05, ±0.07, and ±0.1, respectively.

9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.18 and 0.27 mg/1, recoveries were 101% and 106%, respectively. At concentrations of 4.0 and 5.8 mg/1, the recoveries were 98% and 96%, respectively.

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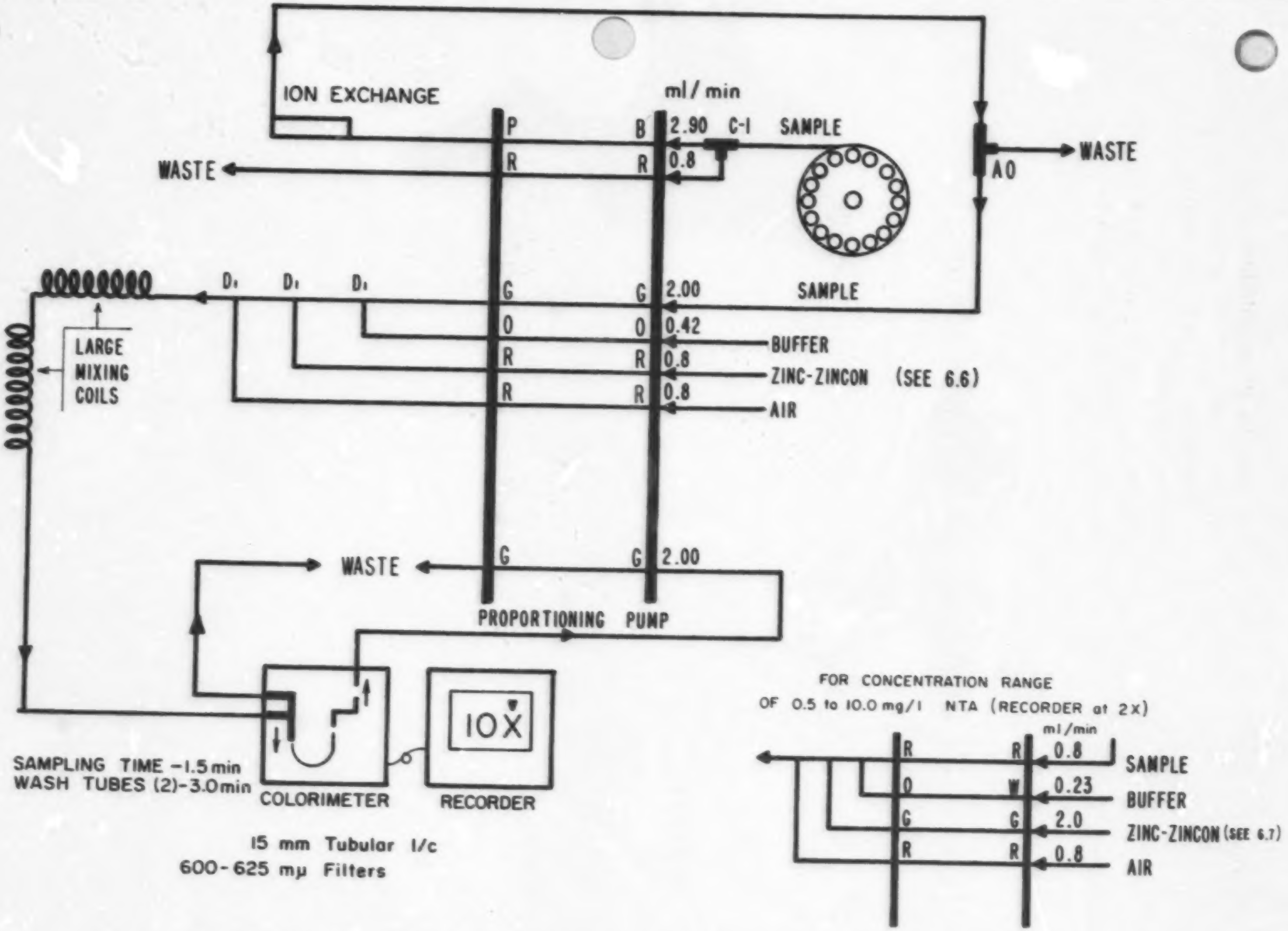
ION EXCHANGE
ml / min
P
B
2.90
C-I
SAMPLE
WASTE
R
R
0.8
WASTE
A O
G
G
2.00
SAMPLE
D₁
D₁
D₁
O
O
0.42
BUFFER
R
R
0.8
ZINC-ZINCON (SEE 6.6)
R
R
0.8
AIR
LARGE MIXING COILS
WASTE
G
G
2.00
PROPORTIONING PUMP
10X
SAMPLING TIME -1.5 min
WASH TUBES (2)-3.0 min
COLORIMETER
RECORDER
15 mm Tubular f/c
600-625 mμ Filters
FOR CONCENTRATION RANGE
OF 0.5 to 10.0 mg/l NTA (RECORDER at 2X)
ml/min
R
R
0.8
SAMPLE
O
W
0.23
BUFFER
G
G
2.0
ZINC-ZINCON (SEE 6.7)
R
R
0.8
AIR

FIGURE 1. NTA MANIFOLD (0.04-1.0 mg/l NTA) AA-I

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